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Interaction Between Charged Macroions In Electrolyte Solution

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By

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Thesis Approval

Interaction Between Charged Macroions In Electrolyte Solution

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Dedication

To Prophet Mohammad Peace Be upon him…….

To my father who is engraved in my memory ……

To my mother……

DECLARATION

I certify that this thesis, which is submitted for the degree of master, is the result of my own research, except where otherwise acknowledged, and that this thesis or any part of the same has not been submitted for a higher degree to any university or institution.

signed:

Mowafaq Khaled I. Hoshieh

Date: / / 2009

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Mowafaq Khaled I. Hoshieh

Abstract

Interactions between two like-charged and unlike-charged Macroions in the presence of their counterions with various amount of simple 1:3 salt confined into a cylindrical cell have been investigated by Monte Carlo simulations. The mean force as a function of Macroion separation has been determined. Without additional salt, a strongly repulsive force was obtained for the 60:1 system, consistent with a stable solution of Macroions. At a trivalent counterion-to–Macroion charge ratio $\beta \approx 0.4$, the mean force became attractive at short separation, but stayed a substantialy repulsion at longer separations. For all systems the attractive However, at stoichiometric amount of trivalent counterions, no long-range repulsion remained and the attraction became substantial. In excess of salt, the magnitude of the attractive force was reduced. For systems with unlike-charged macroions, the attractive force is less than that with like-charged macroions. The attractive component of the mean force originates from spatial correlations between counterions residing near different Macroions and is not captured by mean-field theories such as Poisson-Boltzmann equation or any of its simplifications. The observed sequence of mean-forces are consistent with recent experimental observations on aqueous solution on SDS micelles as $Al\left(NO_3\right)_3$ is added, demonstrating evidence of attractive forces appearing between like-charged colloids induced by multivalent counterions in aqueous solutions.

In this study we were use Monte Carlo simulations, it is easiest to work in the canonical ensemble, just moving particles, not bothering whether the internal energy is changing. We could still just randomly sample the phase space, and calculate the weight of each sampled point. This is not very efficient, since there are usually only few configurations

that significantly contributed to the average. It is possible to visit the configurations corresponding to their weight. This method is called the Metropolis MC method and the algorithm was first introduced in 1953 by Metropolis, Resenbluth, Teller, and Teller (6).

Table Of Contents

List of Figures

List of Definitions

Colloids :any particles which has dimension between 10Å and 10^-6 m (1μ m) .

Surfactant: material that can reduce the surface tension of water when used in very low concentrations .

Micro emulsion :a mixture of water , water insoluble and water transparent liquid.

Physio-chemical :The physical characteristics and chemical composition of a particle in water like particle size , surface charge , hydrophobicity and solvent effects ….etc .

Primitive model : model which both ions and solvent molecules are soft core spheres and the polar nature of the solvent is represented implicitly as a background with a given dielectric constant .

Pmf u(r) : the potential of mean force .

Markov chain : is a sequence of random values whose probabilities at a time interval depends upon the value of the number at the previous time
.
Coion: any of the small ions entering a solid ion exchanger and having the same charge as that of the fixed ions .

Stochastic method : A method that system's subsequent state is determined both by process's prediclable actions and by a random element .

Molsim : is the running program that used, work under unix .

List of Abbreviations

DLVO theory: Derjaguin, Landau, Verwey, and Overbeek theory

rdf"s: radial distribution function

$Z_j = 1$:monovalent counterions

$Z_j = 2$ divalent counterions.

$Z_j = 3$ trivalent counterions

β : Trivalent counterion to Macroion charge ratio.

$F_{ideal}(r)$: Ideal component of the mean force.

$F_{elec}(r)$: Electrostatic component of the mean force.

$F_{hs}(r)$: Hard-Sphere component of the mean force .

SDS micelle: sodium Dodecyl Sulfate micelle

MC: Monte Carlo

NVT: Canonical Ensemble, constant number of particles (N), temperature (T), and volume (V)

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التفاعل بين الايونات في المحاليل الكهرلية

إعداد:موفق خالد إبراهيم الحوشية

إشراف:الدكتورة خولة قمحية

الملخص:

والتي يمكن ان تكون متشابهة او مختلفة في نوع Macroions)ان طبيعة قوى الترابط بين الايونات ذات الحجم الكبير( ) ، Counterionالشحنة وذلك بوجود الايونات الاصغر حجماً ، والمختلفة عن شحنة الايونات كبيرة الحجم والتي تسمى(.Monte-Carloبالاضافة الى تأثير وجود الملح الثلاثي الذرية، يمكن التعرف عليها بواسطة طريقة محاكات الـ فقد تم معرفة مقدار القوة بين هذه الايونات الكبيرة نسبياً ، وكيفية تغيرها بتغير المسافة بين الايونات. فعند عدم وجود الملح الثلاثي الذرية فان هذه القوة تكون قوة تنافر بين هذه الايونات المتشابهة . ولكن مع بدء اضافة هذا الملح الثلاثي الذرية (β)والتي تعرف بـMacroionsوبالذات عندما تكون نسبة شحنة الملح الثلاثي المضاف الى شحنة الايونات كبيرة الحجم ، فان طبيعة القوة بين الايونات الكبيرة تبدأ بالتحول من قوة تنافر الى تجاذب لكنها تبقى تتأثر بتغير المسافة 0.4 تساوي فان قوة التجاذب تصبح اكثر وضوحاً. $\beta = 0.8,1,6$ بين الايونات. ولكن عند زيادة النسبة لتصبح)حول الايونات الكبيرة counterionsان السبب في ظهور قوة التجاذب تلك هو التجمع المكاني للايونات الصغيرة الحجم(مما يعمل على عكس شحنة تلك الايونات وبالتالي تتحول القوة من تنافر الى تجاذب ، فقد ظهر هذا النوع من القوى في . مع العلم أنه لم يرد ذكره في AL(NO3)3)عند اضافة ملح SDSتجارب على محاليل ملحية تحتوي على مايسلات (Poisson-Boltzmann.

)في انظمة تحوي ملح احادي الذرية Macroionsفي هذا البحث تم دراسة والتعرف على هذه القوى بين تلك الايونات ( ) وكذلك التعرف على تاثير اضافة ملح ثلاثي الذرية الى تلك الانظمة Zj=3)وثلاثي الذرية (Zj=2)وثنائي الذرية (Zj=1(على مقدار قوة التجاذب هذه وذلك كعلاقة مع المسافة بين هذه الايونات الكبيرة ، وكان من نتائج البحث ان مقدار قوة التجاذب تلك تزداد مع زيادة تركيز الملح الثلاثي المضاف.

Chapter One

Introduction

Chapter One

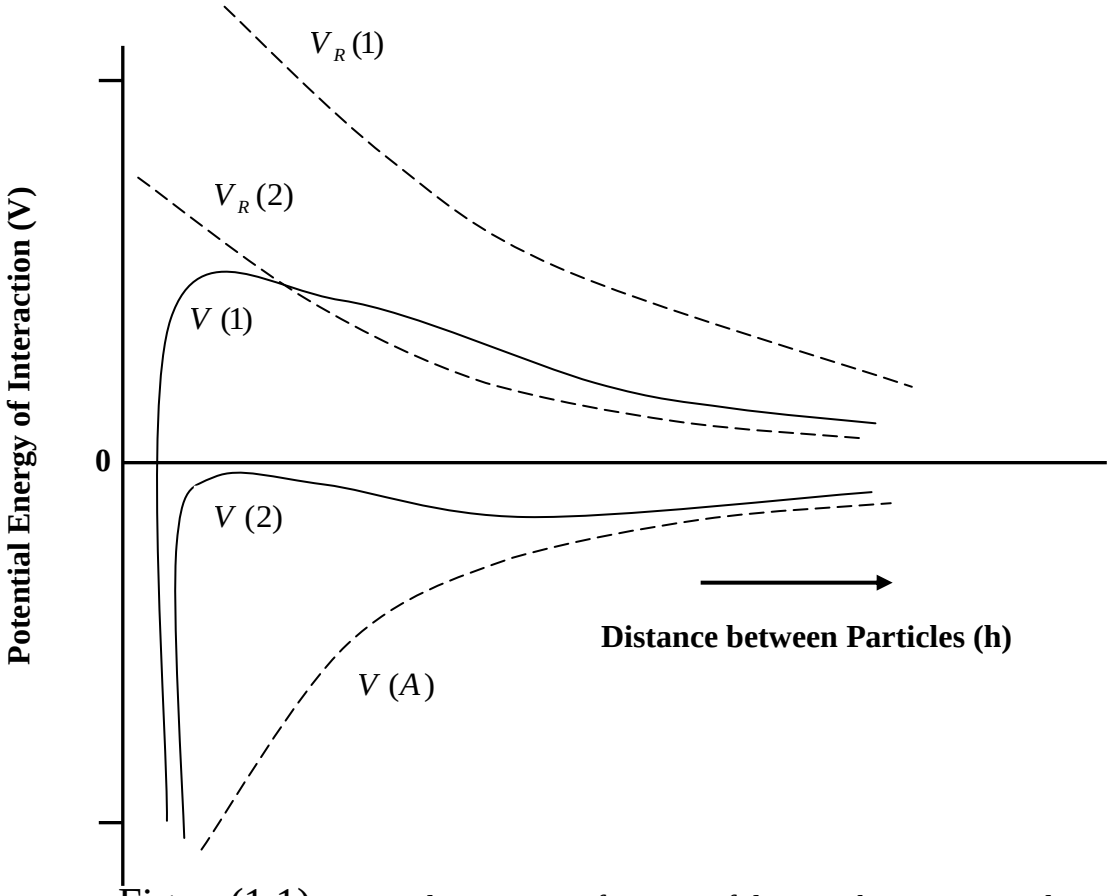
Introduction

Charged Colloids in solution are ubiquitous in a wide variety of biological and technical systems. Some examples are proteins made by amino acids, micelles formed by charged surfactants or charged block copolymers, micro emulsions formed by water, oil, and charged surfactant, silica particles made by silica oxide, and polystyrene based latex particle. In these systems, the physio-chemical properties are to a large degree determined by electrostatic forces. Despite these forces being studied extensively for the last 50 years, the electrostatic interactions in such systems remain a central problem in colloids science (1),(2) .

Water solutions of strongly charged colloidal particles (macroions) with multivalent (Z-valent) counterions (Z–ions) are important in physics, chemistry, biology and chemical engineering. Colloidal particles, charged lipid membranes, DNA, Actin and even cells and viruses are examples of different macroions. Multivalent metallic ions, dendrimers, charged micelles, short DNA and other relatively short polyelectrolyte like spermine can play the role of (Z-ions)(3) .

1.1 DLVO Theory

The classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, predicting purely repulsive forces between like-charged colloidal particles, has often proved satisfactory for explaining the predominant charged stabilization in these systems. It was found that the only attractive force is a Van Der Waals force.(4).



Figure(1.1) Potential energy as a function of distance between particles.

There are, however, several phenomena in solution containing multivalent counterions that cannot be explained using standard mean-field theories. First, the DLVO theory fails to explain the reduced swelling of lyotropic liquid lamellar phases when monovalent counterions are replaced by divalent ones. Second there is experimental evidence that condensation of biopolymers such as DNA or microfilaments can be induced by addition of multivalent ions as trivalent metal ions or polyamines. In addition, there are theoretical studies suggesting electrostatic attractions between like-charged plates, cylindrical or spherical particles in the presence of multivalent counterions. Classical theories are not satisfactory, because they are based on the mean-field approximation, which neglects the spatial correlations among small ions. Several theoretical attempts to account for the correlations effects have been made (4) .

(DLVO) theory was a major theoretical step for rationalization colloidal stability taken in the 1940s. Four decades later, studies using simulation techniques and liquid-state theories demonstrated the existence of an attraction of electrostatic nature between two like-charged planar surfaces originating from ion-ion correlations. Attraction between like-charged macroions of the same origin was later confirmed by several simulation studies and theoretical predicted in the limit of strong electrostatic coupling. In recent paper by Messina(5), he investigated the effects of macroions charge discretization for spherical macroions, where the macroion charges were randomly distributed on the macroion . He employed a spherical cell and reported on the distribution of the counterions with a infinite and on very large electrostatic coupling (5) .

Angelescu and Per Linse considered a cylindrical cell containing two macroions and their counterions only. They examined the cases with valences $Z = {}^{+}1,\ {}^{+}2,\ {}^{+}3$ counterions. These systems have been referred to as the 60:1 , 60:2, 60:3 systems respectively, the mean force and the potential of mean force were given. They also examined the case of adding simple 1:3 salt to 60:1 asymmetric electrolyte system only when the trivalent ions are of opposite charge to the macroions (4).

1.2 Charge Inversion

Several interesting, counterintuitive phenomena have been discovered in such a system, such as charge inversion. Charge inversion happens in a water solution when a macroion binds so many Z-ions that its net charge changes sign. This phenomena is especially important for negative DNA (playing the role of macroion) which should be inverted by positive Z-ions to approach a negatively charged cell membrane. Here we actually assume that the membrane is weakly charged and therefore its charge is not inverted. The question is what happens if the charge of the membrane is also inverted by positive Z-ions. Can DNA still be attracted to the membrane? A similar question was put forward by the recent atomic force experiment designed to verify the theory of charge inversion based on strong correlations between Z-ions (8) , (9) ,(10) .

In the experiment forces between a negatively charged spherical macroion attached to the cantilever (probe) and a positively charged surface were measured at different concentrations of positive Z-ions. (see fig. 1.2a) (9) .

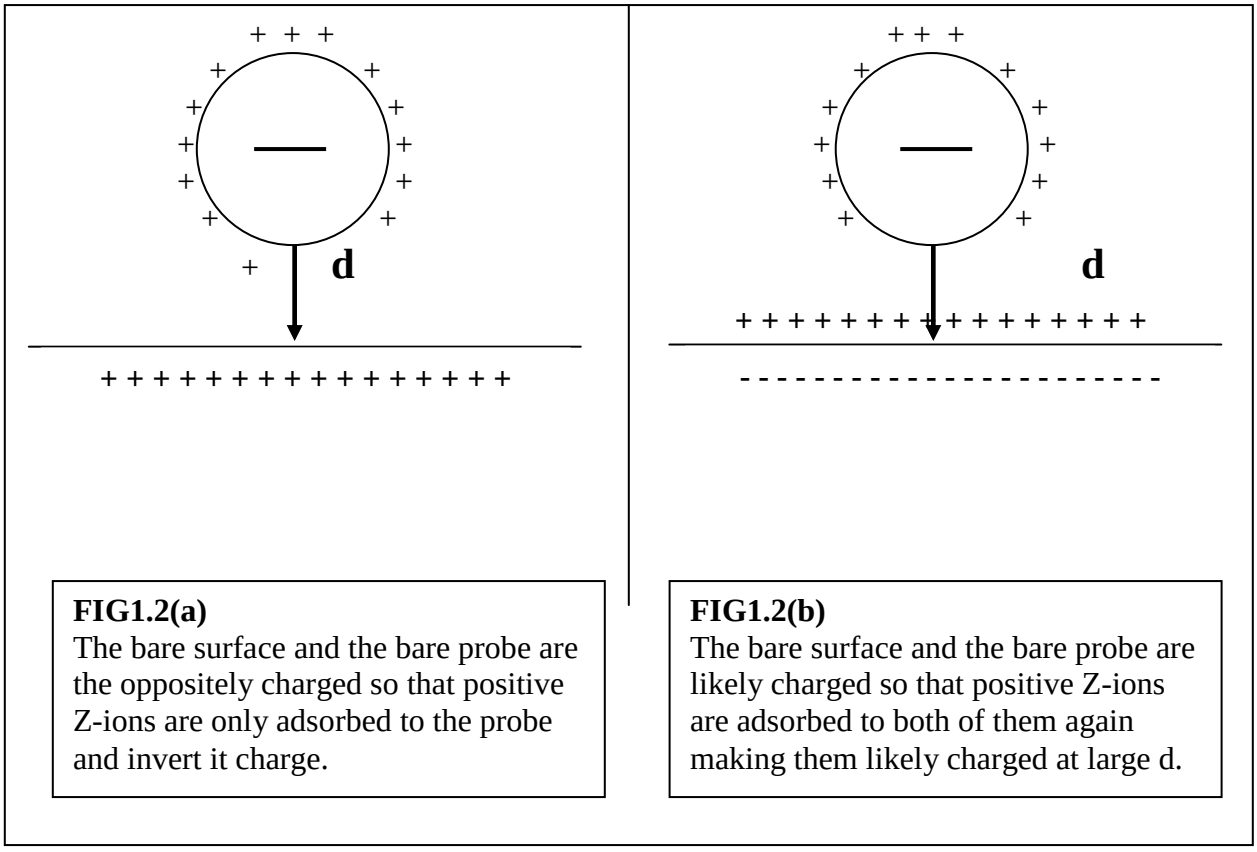


FIG1.2(a)
The bare surface and the bare probe are the oppositely charged so that positive Z-ions are only adsorbed to the probe and invert it charge.

FIG1.2(b)
The bare surface and the bare probe are likely charged so that positive Z-ions are adsorbed to both of them again making them likely charged at large d.

Figure.1.2 Schematic illustration of two experimental setups for atomic force measurements of like charged Macroions. The force between the prob (the big sphere with negative charge) and the surface is measured at different concentrations of Z-ions (small sphere with positive charges).

Increasing concentration of Z-ions the charge of the probe gets inverted by Z-ions and measured force at large (d) becomes repulsive, where (d) is the distance of closest proximity from the probe to the surface.

However, an interesting new feature of the repulsive force was observed, as (d) decreased. The repulsive forces reaches a maximum at d □ 100Å and start to decrease. This suggests the existence of a competing attraction. One can also consider different experimental setup(3) in which the probe and the surface are likely charged and both adsorb Z-ions (fig.

1.2.b).When the concentration of Z-ions is high enough so that the charges of the surface and probe are both inverted at large (d), it is interesting to find out whether the force may be attractive. Preliminary experiments showed such attraction (3).

Rui Zhang *et.al* (8) focused in their study on the case of two bare negatively charged macroions and positive Z-ions corresponding to fig.1.2.b since it is pedagogically simple. They assumed that the valence of Z-ions, Z>>1 but still many Z-ions are needed to neutralize one macroion. The two macroions were spherical but different in their bare surface charge densities. Actually this was the reason why this attraction was not reported before, when the focus was on identical macroions (8) .

1.3 The Canonical Ensemble (NVT)

One basic concept in statistical thermodynamics is the ensemble. Members of an ensemble, fulfill some constraints, which are specific for that ensemble. These constraints thermodynamically describe the system completely.

In the canonical ensemble, which is used in this study, the number of particles (N), the temperature (T), and the volume (V) are kept constant. This has the consequence that the configurational states are not all equally likely anymore. The probability of a certain state occurring is related to its energy. States with low energy are more likely to occur than configurations with high energy. This is because the system is now allowed to exchange heat with a thermostat, and the number of possible states for our system plus the thermostat has to be counted(6).Lobskin and Qamhieh have performed fluid simulations of solutions of the 60:1 system with different amount of added salt (8) .

1.4 Objectives

In this work we want to study the interaction between two like and unlike charged macroions in the presence of large concentration of Z-ions and comparing it with the like ones . This can be done by performing tailored Monte Carlo simulations corresponding to the experimental observations of $SDS-AL(NO_3)_3-H_2O$ system, and using a very simplified approach where the mean force between two micelles can be determined at different

conditions using the primitive model(4). Also the force components, the ideal $F_{ideal}(r)$, the electrostatic $F_{elec}(r)$ and hard-sphere $F_{hs}(r)$ mean force are calculated .

The distribution of small ions near a macroion will be examined by determination of macroion – small ions radial distribution functions.

Chapter Two

Models and methods

2.1 Force and Potential

The principal property of interest in this study is the mean force $F(r)$ and the corresponding potential of mean force $\bigcup_{pot}(r)$ acting on one of the macroions at macroion separation r. The mean force F operating on macroion M, projected on the macroion – macroion inter particle vector r(4) , is defined by:

$$F(r) \equiv \sum_{i=M}^{N} \left\langle -\nabla_{rMi}\ U_{Mi}(r_{Mi}) \right\rangle, \ldots\ldots\ldots\ldots \quad (1)$$

Where N is the number of particles in the electroneutral system .

With $F(r) > 0$ implying a repulsive and $F(r) < 0$ an attractive mean force and $\langle \ldots\ldots\ldots \rangle$ denoting an ensemble average over the positions of the small ions. The related $U^{pmf}(r)$ is defined as:

$$U^{pmf}(r) \equiv -\int_{-\infty}^{r} F(r')dr'. \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

At sufficiently large r, $F(r)\ and\ U(r)$ approach zero. Both quantities depend on (i) the direct repulsive macroion-macroion interaction $U_{MM}(r)\ and\ (ii)$ and indirect contribution mediated by the small ions.

At least two independent routes exist to determine the interaction between the macroions. Firstly by sampling the frequency of the macroion separation r, the pmf is readily available through $U^{pmf}(r)/KT = -\ln\left[P(r)/P(r \to \infty)\right]$ and the mean force from equation(2). Second, in separate simulations with fixed macroion separations, the mean force can be sampled using expressions originating from equation (1),(4) .

From a force balance, equation (1) can be reformulated into different, but equivalent expressions, possessing different numerical efficiencies(4).

In this work, the mean force is divided into three terms according to:

$$F(r) = F_{ideal}(r) + F_{hs}(r) + F_{elec}(r) \text{.....(3)}$$

Where:

$$F_{ideal}(r) = A\,KT \sum_{i}^{small\ ions} \left[P_i(Z=0) - P_i(Z = L_{cyl}/2) \right], \text{.....(4)}$$

$$F_{hs}(r) = \sum_{i<j}^{N} {}' \left\langle -\nabla r_j\, U_{ij}^{hs}(r_{ij}) \right\rangle, \text{ .....(5)}$$

And

$$F_{elec}(r) = \sum_{i<j}^{N} {}' \left\langle -\nabla r_{ij}\, U_{ij}^{elec}(r_{ij}) \right\rangle, \text{ .....(6)}$$

With $F_{ideal}(r)$ arising from the difference in the transfer of linear moments of the small ions across the planes Z=0 and $Z = \underset{cyl}{L}/2$ whereas $F_{hs}(r)$ and $F_{elec}(r)$ are average forces appearing across the plane Z=0 originating from the hard-sphere repulsion among the small ions and the electrostatic interaction among all charged particles, respectively. In equation (4), $(P_i(Z = Z'))$ denotes the number density of the small ion species i in the plane $Z = Z'$ averaged over the cylindrical cross section area A, and in equation (5) and equation (6) the $(')$ in the summation denotes that only pairs of particles located at different sides of the plane Z=0 should be considered. As long as $r << \underset{cyl}{L}/2$, $F_{ideal}(r)$ is dominated by the $P_i(Z=0)$ term. (4).

It should be noted that we are calculating the mean force and not the effective force on a macroion. In the corresponding fluid, the macroion-macroion mean force is the force acting between two macroions averaged over the positions of surrounding small ions and macroions, whereas an effective N-body force among N macroions is averaged over the positions of

surrounding small ions only. The effective N-body force is frequently approximated by a pairwise sum of effective pair forces. The same holds for the potential. In the present systems with attractive macroions-counterion interactions, $F_{ideal}(r)$ becomes repulsive at short macroion separation because of an accumulation of counterions in the region between the macroions. The hard-sphere contribution $F_{hs}(r)$ is always positive and becomes important at large concentration of small ions. Finally $F_{elec}(r)$ is normally attractive, but it can be repulsive as well (4).

2.2 Monte Carlo Simulation

Monte Carlo (MC) simulation is a stochastic method, which enables us to solve (multidimensional) integrals. It has its name from the use of random numbers in the algorithm (6) .

When using Monte Carlo simulations, it is easiest to work in the canonical ensemble, just moving particles, not bothering whether the internal energy is changing. We could still just randomly sample the phase space, and calculate the weight of each sampled point. This is not very efficient, since there are usually only few configurations that significantly contributed to the average. It is possible to visit the configurations corresponding to their weight. This method is called the Metropolis MC method and the algorithm was first introduced in 1953 by Metropolis, Resenbluth, Teller, and Teller (6).

2.2.1 The Metropolis Algorithm

In the Metropolis algorithm, the phase is sampled in such a way that configurations that contribute significantly to the configurational integral are visited more frequently than those that only contribute little to it. Acceptance and rejection of MC trial move are chosen in away that produces a Markov chain (6) . It is implemented using the following algorithm:

1- Chose the particles to move at random and move them by a (random) distance.

2- Calculate the energy difference $\Delta U_{trial} = U_{new} - U_{old}$ between the old and the new configuration.

3- If $\Delta U_{trial} \leq 0$ accept the new configuration, else if random number generating $0 \leq £ \leq 1$, and smaller than $\exp(-\Delta U_{trial} / RT)$, accept the move, else reject the move and count the old configuration as the new configuration. After every step , data for averages is accumulated before a new trial move is attempted (6). See Figure. 2.1

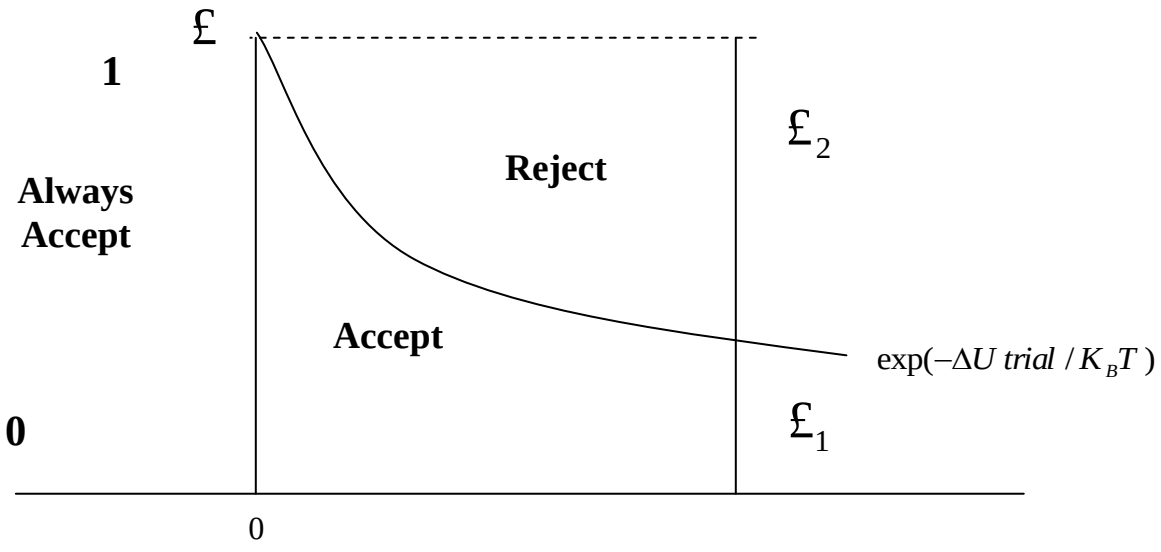


Figure.2.1: Scheme of accepting and rejecting trial moves in Metropolis algorithm.

2.3 The Model

The model system under consideration represents an aqueous solution of charged micelles. The Micelles are described as charged hard spheres referred as macroions, each of them carrying a bare charge of $Z_m = -60$ au and having the radius $R_M = 20A^\circ$. The monovalent counterions and the salt species referred to as small ions are also represented as charged hard-sphere. Since the cations of the salt differ from the counterions originating from the surfactant, two types of counterions with valences $Z_j = {}^{+}1$ and $Z_I = {}^{+}3$ are present. The coions originating from salt are always monovalent $Z_c = {}^{-}1$. All small ions have the radius $2A^\circ$.

The monomeric surfactants present in real micellar solutions are omitted, and the moderate salt- induced micellar growth is neglected. The solvent is treated as a dielectric continuum and enters the model only through its relative permittivity. Surface polarization at the surfaces of the macroions is neglected.

In the present work, we consider a cylindrical cell possessing hard walls containing two like charge of $Z_m = -60$ and unlike charge of $Z_m = -90$, $Z_m = -30$ and the corresponding amount of small ions constituting an electro neutral system. Throughout the cylinder radius $R_{cyl} = 80A^\circ$ and the length $L_{cyl} = 398A^\circ$ have been employed. Also a spherical cell of radius $100A^\circ$ containing one macroion and appropriate number of small ions has been employed. The radius of sphere is $20A^\circ$ and all small ions are of $2A^\circ$ radius. Both systems have a temperature 298 K and pressure of 0.1013 Pa.

The reference salt-free monovalent counterion 60:1 (Z=1), divalent counterion 60:2 (Z=2) and trivalent counterion 60:3 (Z=3) will be examined first and the case of added simple 1:3 salt (I-ions), where the trivalent ions are of opposite charge to the macroions, will be added

to 60:1, 60:2 and 60:3 systems. Consequently the trivalent counterion charge – to – macroion ratio $\beta = |N_I Z_I| / |N_M Z_M|$ ranges between zero and 6.25. We have focused on the mean force and the potential of mean force, also the radial distribution functions (rdf's) correspond to the distribution of ions near a single macroion, providing the relative densities of small ions at distance r from the macroions, have been examined in the spherical cell.

We have first made equilibration to start configuration then we continue equilibration run with (10^5) steps/ passes to find the mean force. But for radial distribution function we run the molsim(11) program ($5*10^5$) steps/ passes .

Chapter Three

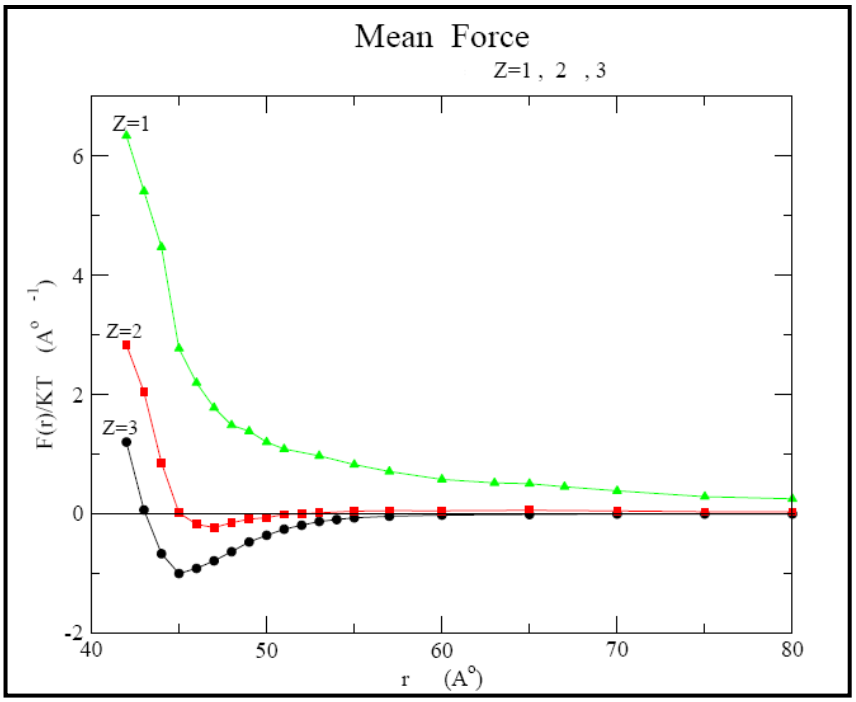
Results And Discussion

Before considering the effect of adding salt on the mean force acting on the macroion, the corresponding mean forces without salt but different valences of the counterions will be presented for reference purposes. The system with two like and unlike charge macroions in cylindrical cell will first be examined. Thereafter, the properties of systems with one macroion in spherical cell will be assessed.

3.1 Salt Free Solution:

Consider a cylindrical cell containing two like charge macroions and their counterions (j-ions) only. The cases with $Z_j = +1, +2 \; and \; +3$ will be examined, and these systems will be referred to as the 60:1 , 60:2, and 60:3 systems, respectively. The other conditions are as given in the model section. The mean force $F(r)/KT$ for 60:1 , 60:2, and 60:3 systems, as a function of macroion separation r is shown in figure 3.1 The surface – to – surface separation of the two macroions are given by $r - 2R_M = r - 40A^\circ$.

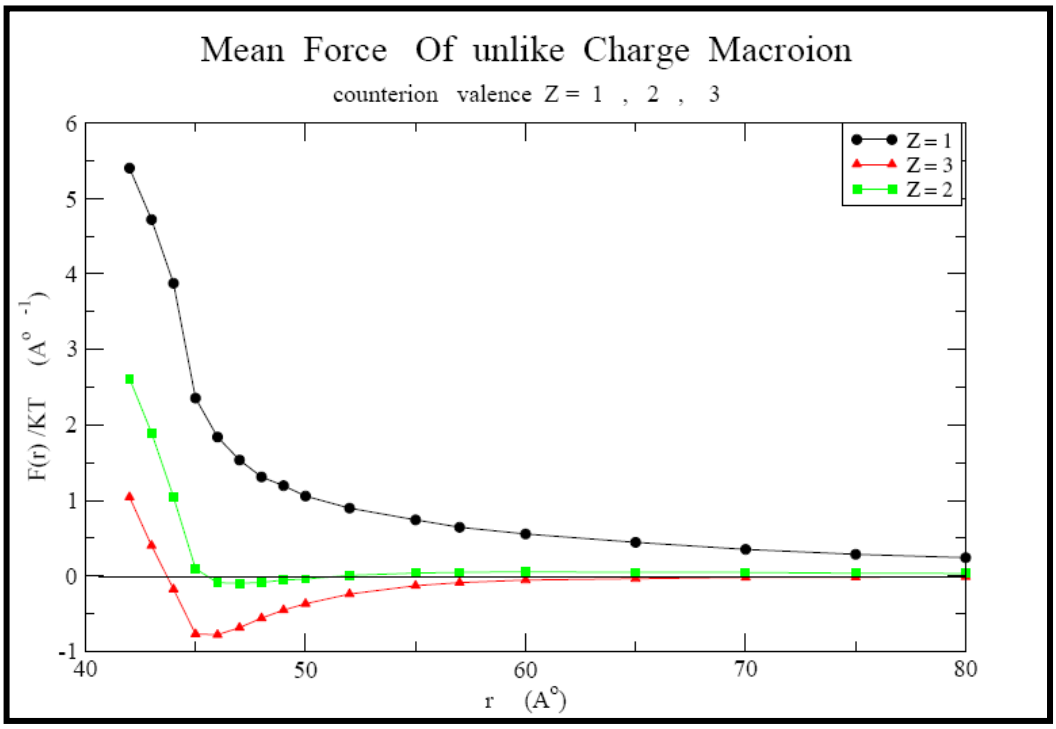
Figure 3.1 shows that the qualitative behavior of the mean force is strongly dependent on the counterion valence. With monovalent counterions $Z = +1$, the mean force becomes increasingly more repulsive as the separation between the two macroions is reduced with the repulsion starting at large separation. On the contrary, with trivalent counterions $Z = +3$ the mean force becomes increasingly more attractive as the separation is reduced, but the attraction appearing only at relatively short separations $43A^\circ < r < 58A^\circ$.



Figure(3.1) Mean force $F(r)/kT$ of like charged Macroions as a function of the Macroions separation r for the 60:1 (Z=1), 60:2(Z=2) and 60:3 (Z=3) systems.

At very short separation $r < 43A^{\circ}$ the force becomes less attractive and even repulsive owing to the overlap of the very thin double layers of the two macroions, and at $r < 43A^{\circ}$ the remaining monolayer in the region between the two macroions starts to be expelled. With divalent counterions, an intermediate and richer behavior is found. At $r \geq 56A^{\circ}$ the force is weakly repulsive, at $45A^{\circ} < r < 56A^{\circ}$ the force is attractive, and finally at very short separation, $r < 45A^{\circ}$ the force becomes repulsive again.

The mean force for the (Zj=1) , (Zj=2) , and Zj=3) systems of unlike charge macroions (Z_{M1} = - 30 and Z_{M2} = - 90) as a function of the macroions separation (r) is shown in figure 3.2, with the conditions being as given in the model section. The separation distance (r) is given from center – to – center of the two macroions. Figure 3.2 shows that the mean force is also strongly dependent on the counterion valence as like charge macroions.



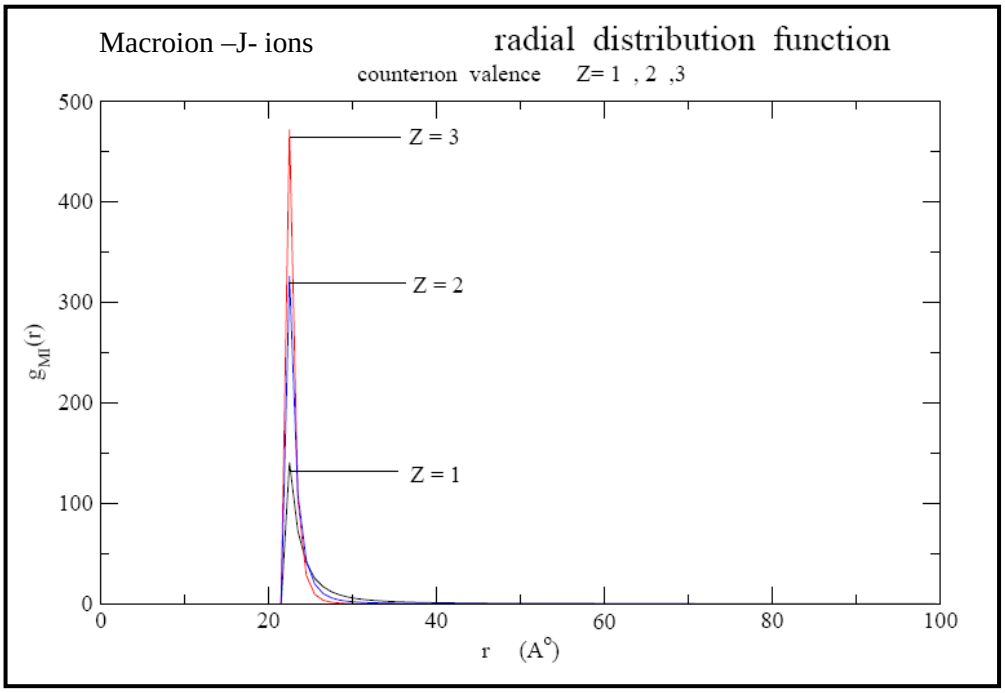
Figure(3.2) Mean force of unlike-charged Macroion as a function of the Macroion separation r for the 60:1 (Z=1), 60:2(Z=2) and 60:3 (Z=3) systems.

With monovalent counterions $Zj = +1$, the mean force becomes less repulsive as the separation between the two macroions is increased.

But with trivalent counterions $Zj = +3$ the mean force becomes increasingly more attractive as separation is reduced, but the attraction appearing only at relatively short separations. At $r < 44A^{\circ}$ the force becomes less attractive and becomes repulsive because of the overlap of the double layers of the two macroions.

With divalent counterions ($Zj = +2$), the mean force is intermediate behavior is founded. At $r \geq 52A^{\circ}$ the force is weakly repulsive, at $44A^{\circ} < r < 52A^{\circ}$ the force is attractive, and finally at very short separation $r < 44A^{\circ}$ the force becomes repulsive again. We note that the mean force of unlike charge macroions is less attractive than of the mean force of like charge macroions at $43A^{\circ} < r < 56A^{\circ}$ region.

In this analysis the macroions-counterion radial distribution function (rdfs) for the central charge distribution with different counterions valences are showing in figure 3.3 Such (rdfs) obtained from a spherical cell describe the distribution of counterions near a single macroion. The function provides the relative density of small ions at distance (r) from the macroion, its value being unity in the absence of any spatial correlations. Independent of the counterion valence, there is strong accumulation of the counterions near the macroion surface. At increasing counterion valence, the macroion-counterion electrostatic increases in magnitude, leading to a more uneven counterion distribution. The values of the g_{Mj} at macroion –counterion hard-sphere contact $r = 22A^{\circ}$ $are\ 140, 310, and\ 480$ with $Z_j = 1, 2, and\ 3$, respectively. The macroion-counterion (rdfs) of $Z_j = 1, 2, and\ 3$ have maxima at the hard-sphere contact separation $r = R_m + R_s = 22A^{\circ}$ as shown in figure 3.3.

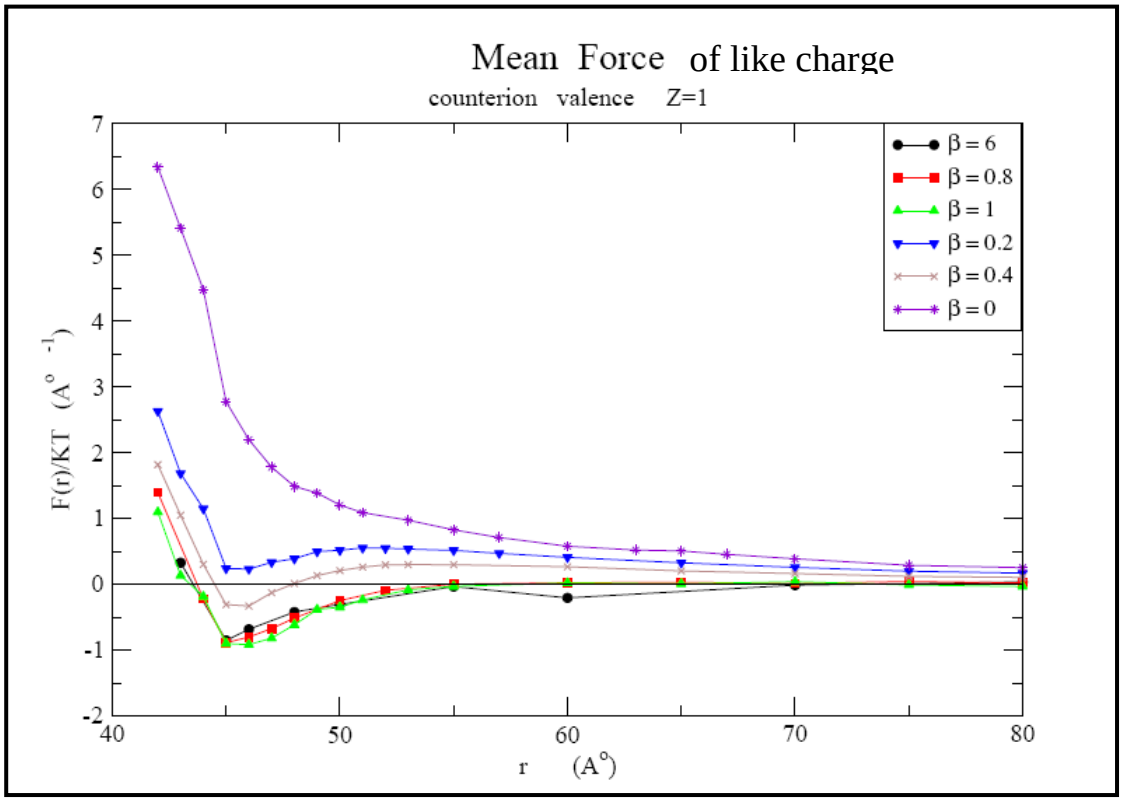


Figure(3.3) Macroion-counterion radial distribution function of the 60:1 (Z=1), 60:2(Z=2) and 60:3 (Z=3) systems as a function of Macroion-counterion r.

3.2 Salt Added

Let us now consider the 60:1 asymmetric electrolyte system at various amount of added simple 1:3 salt, where the trivalent ions are of opposite charge to the macroions in the cylindrical cell. The largest amount of simple salt corresponds to trivalent counterion charge-to-macroion charge ratio $\beta = 6$.

Figure 3.4 displays the mean force as a function of the macroion separator $r\,at$ different amounts of salt. As the amount of the simple 1:3 salt is increased, we note that the repulsive mean force initially decreases at all separations, the effect being most prominent at short separation, then becomes attractive starting at $r \approx 43A^{\circ}$. Thereafter the magnitude of the attraction as well as the extension of attraction increases and simultaneously the repulsion at long separation vanishes. Finally the magnitude of the attractive force decreases .



Figure(3.4) Mean force $F(r)/kT$ of like–charged Macroions as a function of the Macroion separation r of 60:1(Z=1) system at indicated amount of simple 1:3 added salt expressed by the trivalent counterion charge – to – Macroion charge ratio β = 0, 0.2, 0.4, 0.8, 1, and 6.

In more detail, only a small amount of salt is necessary for the large initial reduction of the repulsive force. Moreover, the onset of attraction at short separation appears already at $\beta = 0.4$, and the maximal attraction appears near $\beta = 1$. At $\beta = 6$, the force is similar to that at $\beta = 0.8$. For not too small β, there is a strong upturn of the mean force at $r < 43A^{\circ}$.

The mean force of the 60:1 system at $\beta = 1$ in figure 3.4 and 60:3 system in figure 3.2 are very similar since the 60:1 system at $\beta = 1$ can be viewed as an addition of a 1:1 electrolyte to the 60:3 system, and the additional 1:1 electrolyte has thus only a very marginal screening on the attractive mean force.

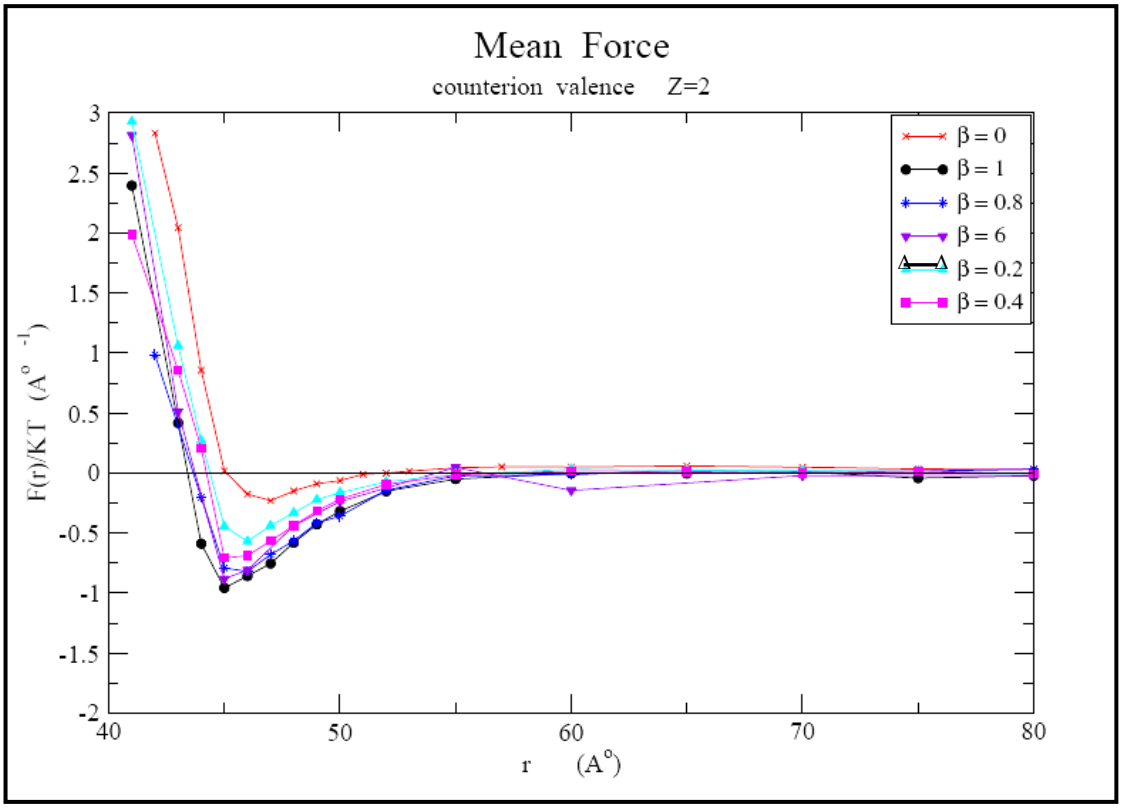
Moreover, the force of the 60:1 system at $\beta = 0.4$ in figure 3.4 resembles that of the 60:2 system in figure 3.2, an attractive at short separation and a long-range repulsion of large separations are common features.

For 60:2 ($Z_j = 2$) asymmetric electrolyte system at various amount of added simple 1:3 salt, also the trivalent counterions (I-ion) are of opposite charge of the macroions.

The trivalent counterion charge-to-macroion charge ratio $\beta = 0, 0.2, 0.4, 0.8, 1, and\ 6$ values.

The mean force as a function of the macroion separation (r) is shown in figure 3.5 for the 60:2 ($Z_j = 2$) asymmetric electrolyte system at various amount of added simple 1:3 salt.

The mean force is attractive for all β values at $43A^{\circ} < r < 55A^{\circ}$. The magnitude of the mean force reduces after $r \geq 55A^{\circ}$. Moreover the attraction appears at $\beta = 0$ and the maximal attraction appears near $\beta = 1$. At $\beta = 6$ the force is similar to that at $\beta = 0.8$. The mean force of 60:2 system at $\beta = 1$ in figure 3.5 and of the 60:3 system in figure 3.1 are very similar. We can also not that the mean force of 60:2 system at $\beta = 0$ and of the 60:2 system in figure 3.1.



Figure(3.5) Mean force $F(r)/kT$ of like-charged Macroion as a function of Macroion separation r for 60:2 (Z=2) system at β = 0,0.2,0.4,0.8,1 and 6.

Now consider the 60:3 $(Z_j = 3)$ asymmetric electrolyte system at various amount of added simple 1:3 salt, the trivalent ions (I-ions) are of opposite charge to the macroions. As well as in previous system the trivalent counterion charge-to macroion charge ratio β has

values $0, 0.2, 0.4, 0.8, 1, and\ 6$. Figure 3.6 shows that at $\beta = 0$ the mean force becomes more attractive than of its values of 60:1 and 60:2 systems. We note that the repulsive mean force hardly decreases at $r < 43A^{\circ}$, then it becomes attractive at $r > 43A^{\circ}$. It has a maximal attraction at $r \approx 45A^{\circ}$, then its magnitude reduces at $r > 46A^{\circ}$, We can see that the magnitudes of the attractive mean force become closer to each other at $\beta > 0$.

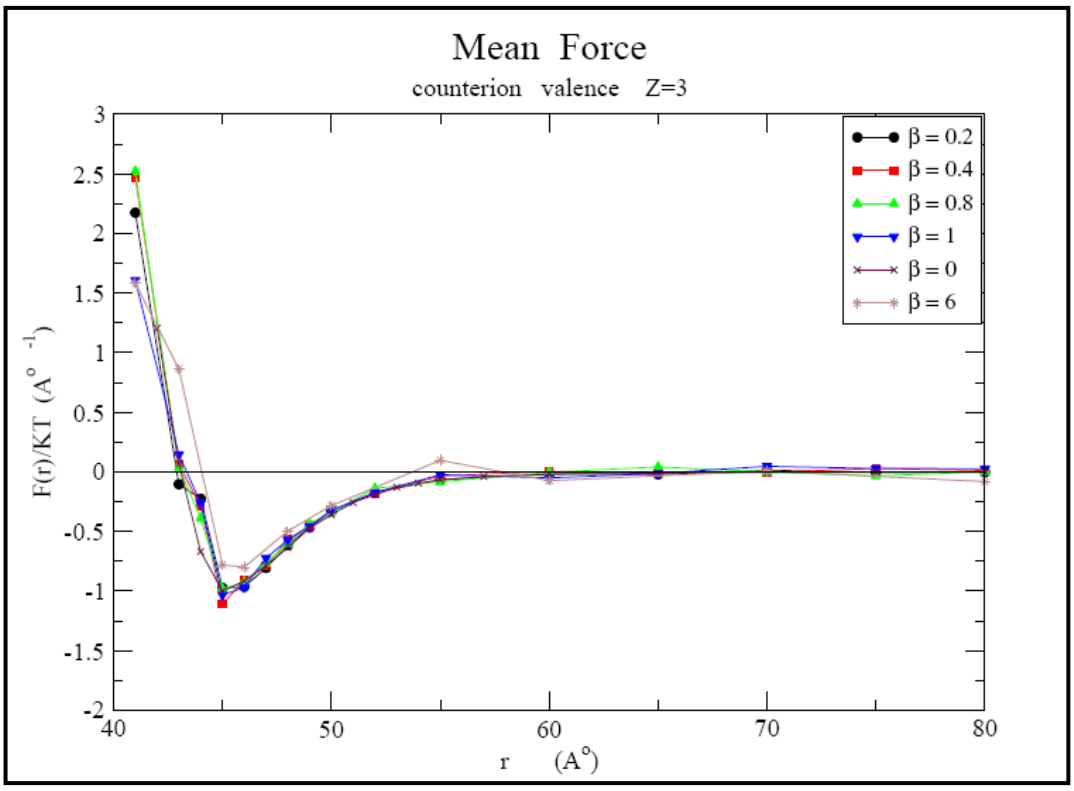
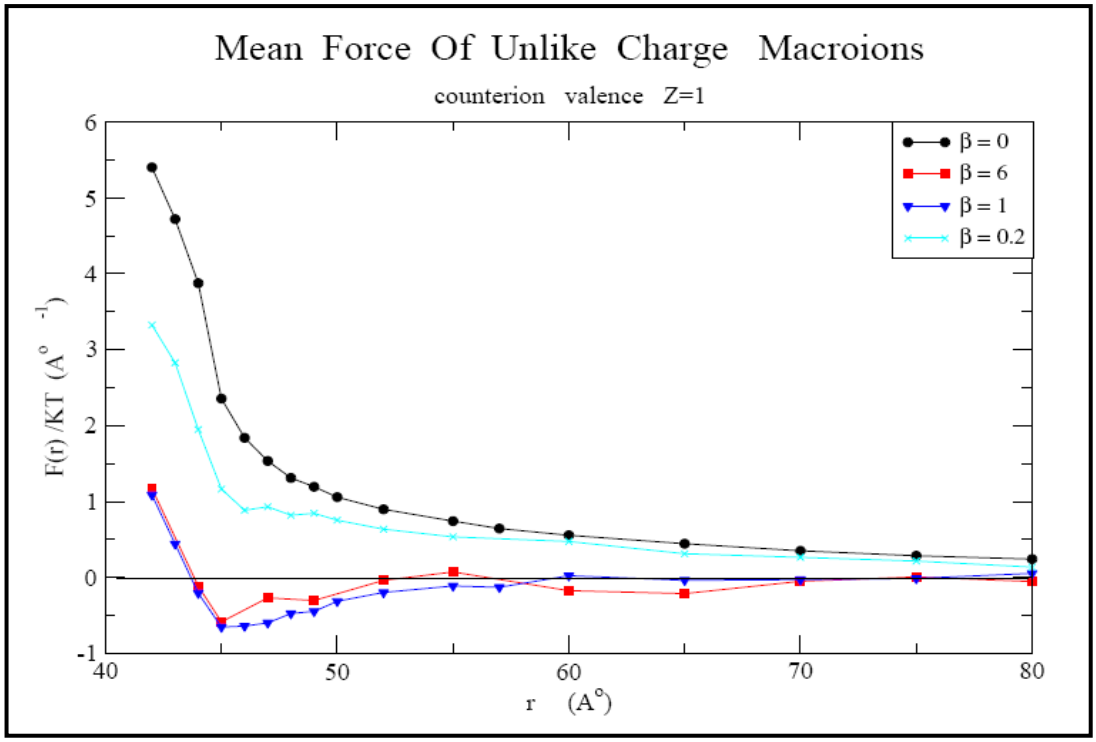


Figure (3.6) Mean force $F(r)/kT$ of like-charged Macroions as a function of Macroion separation r for 60:3 (Z=3) system at β = 0,0.2,0.4,0.8,1 and 6.

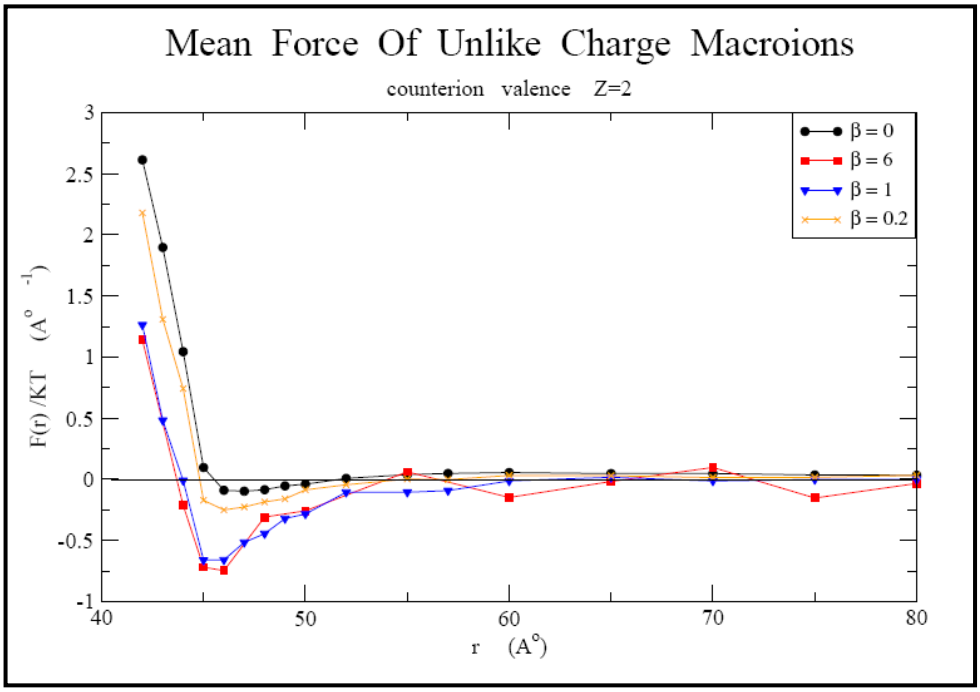
The mean force of unlike-charge macroions (Z_{M1} = -30, Z_{M2} = -90) of $Zj = +1$ asymmetric electrolyte system at various amount of added 1:3 salt as a function of the macroion separation (r) is shown in figure 3.7 .



Figure(3.7) Mean force $F(r)/kT$ of unlike-charged Macroions as a function of Macroion separation r for 60:1 (Z=1) system at $\beta = 0, 0.2, 0.1$ and 6.

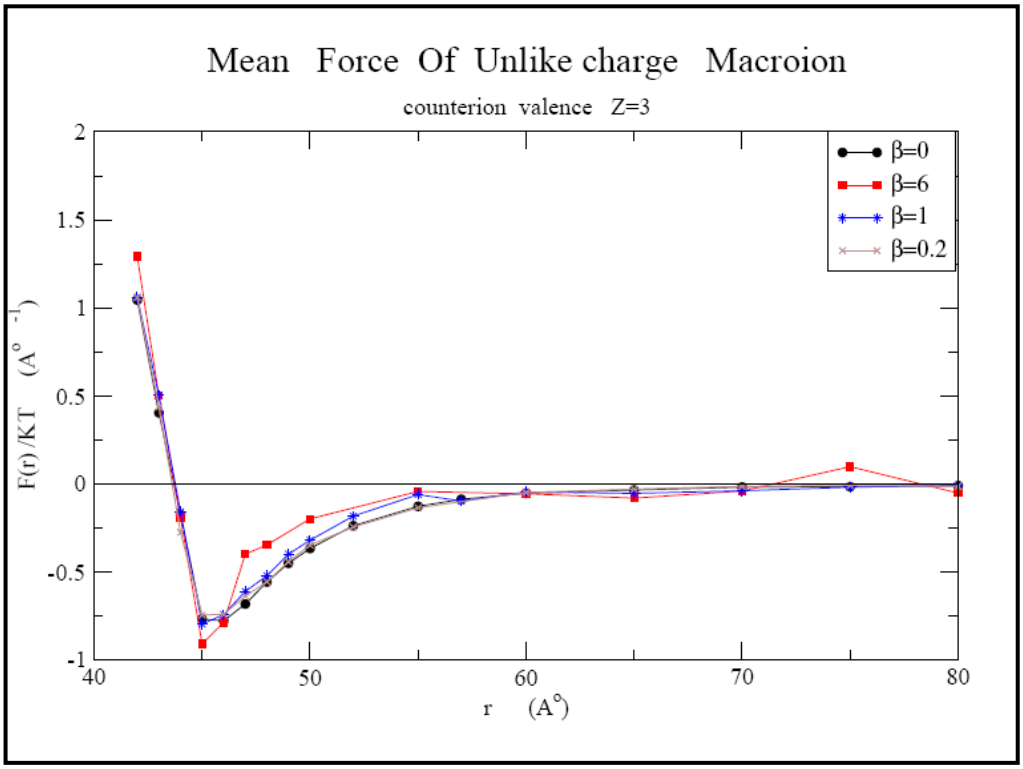
As the amount of the salt is increased the repulsive mean force initially decreases at all separation, then it becomes attractive starting at $r \approx 43A^{\circ}$, thereafter the magnitude of the attraction as well as the extension of attraction increases and simultaneously the repulsion at long separation vanishes, finally the magnitude of the attractive force reduces. Moreover, the appearance of attraction at short separation is at $\beta = 6$ and $\beta = 1$, and the maximal attraction appears near $\beta = 1$ at macroion separation $r = 45A^{\circ}$. We see that for $\beta = 0$ and $\beta = 0.2$ the mean force is clearly repulsive. The mean force of the 60:1 system at $\beta = 1$ in figure 3.7 and of the 60:2 without salt system in figure 3.2 are very similar. Since the 60:1 system at $\beta = 1$ can be viewed as an addition of a 1:1 electrolyte to the 60:3 system in fig 3.2. We also note that the mean force of the 60:1 system at $\beta = 0$ resembles that of 60:1 system in figure3.2 .

Figure 3.8 shows the mean force of 60:2 system with added 1:3 simple salt. The mean force of unlike-charge macroions is attractive for $\beta = 0$, 0.2, 1 and 6 at macroion separation $43A^{\circ} < r < 53A^{\circ}$. At very short separation $r > 43A^{\circ}$ the force is repulsive for all β values. The attractive mean force has a maximal value at $\beta = 6$. The attractive mean force is gradually increase as β increase as shown from figure 3.8. The magnitude of the attractive mean force reduces at $r > 53A^{\circ}$.



Figure(3.8) Mean force $F(r)/kT$ of unlike-charged Macroion as a function of Macroion separation r for 60:2 (Z=2) system at β= 0,0.2,0.1 and 6

For the system of 60:3 asymmetric electrolyte with added 1:3 salt, the mean force of unlike-charge macroion with different amount of trivalent counterion charge-to- macroion charge ratio $\beta = 0, 0.2, 1, 6$ is shown in figure 3.9 .

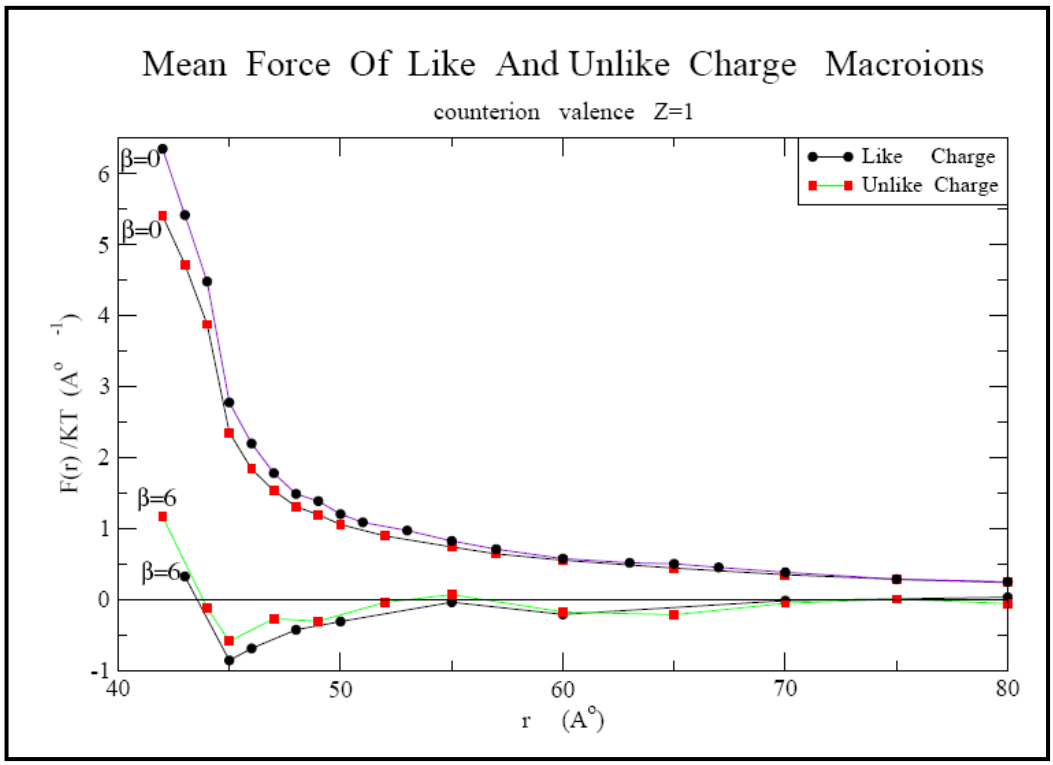


Figure(3.9) Mean force $F(r)/kT$ of unlike-charged Macroion as a function of Macroion separation r for 60:3 (Z=3) system at β = 0,0.2,1 and 6.

Initially the repulsive mean force decreases at all separation and becomes attractive between $44A^{\circ} < r < 60A^{\circ}$. Moreover the onset of attraction at short separation appears at small β values. We note from the figure 3.9 that the maximum value of the mean force at $\beta = 6$. All attractive mean force at all β ratio have values close together as shown by figure 3.9 .

A comparison between the mean force of the like and unlike charge macroions in cylindrical cell of 60:1 system at various amount of added simple 1:3 salt has been shown in figure 3.10 . For both like and unlike charged macroion the counterion charge-to macroion charge ratio $\beta = 0$, the mean force is clearly repulsive, but it decreases at all separations with the effect being most obviously noted at short ones .

For $\beta = 6$ the mean force becomes attractive for both like and unlike charge macroions starting at $r \approx 43A^{\circ}$. It has a maximal value between $43A^{\circ} < r < 52A^{\circ}$, thereafter the magnitude of the attraction as well as the extension of attraction increases.



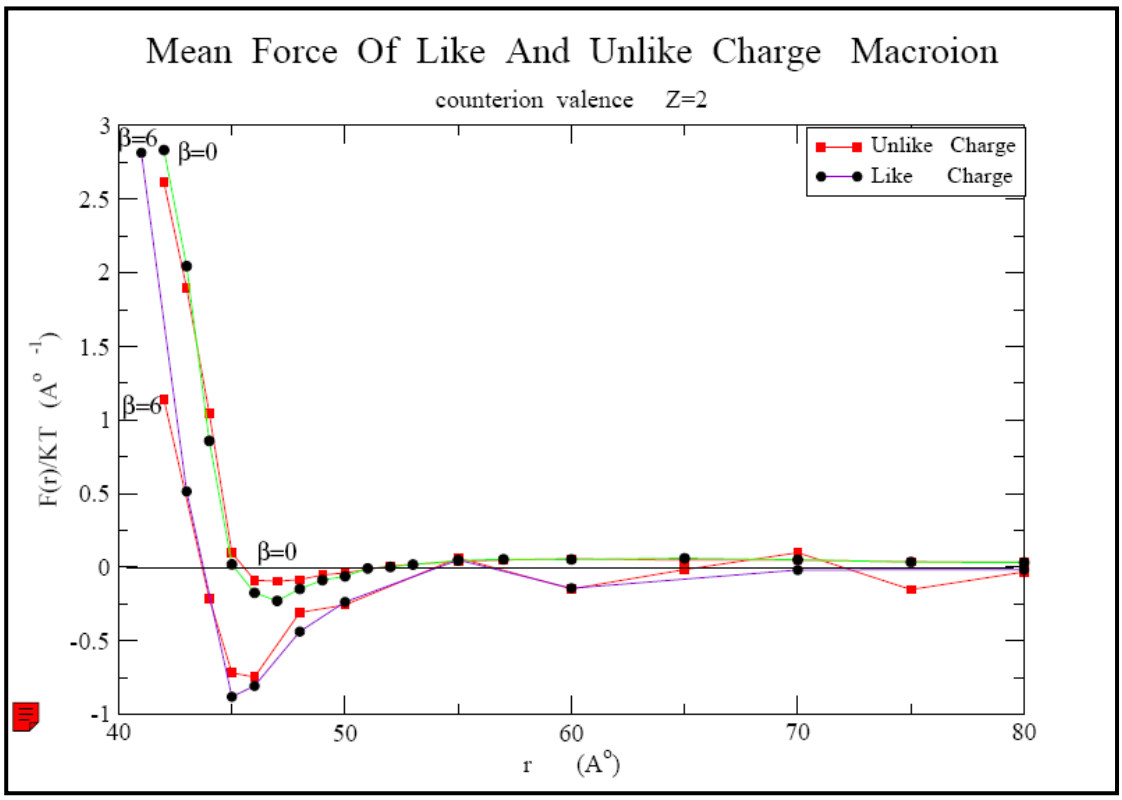
Figure(3.10) M

Finally the magnitude of the attractive force reduces at $r > 53A^{\circ}$.

We have noted the prominent effect of 1:3 added salt to the 60:1 system. The attractive mean force of like charged macroions for $\beta = 6$ is more than the attractive mean force of unlike charged macroions.

Macroion separ

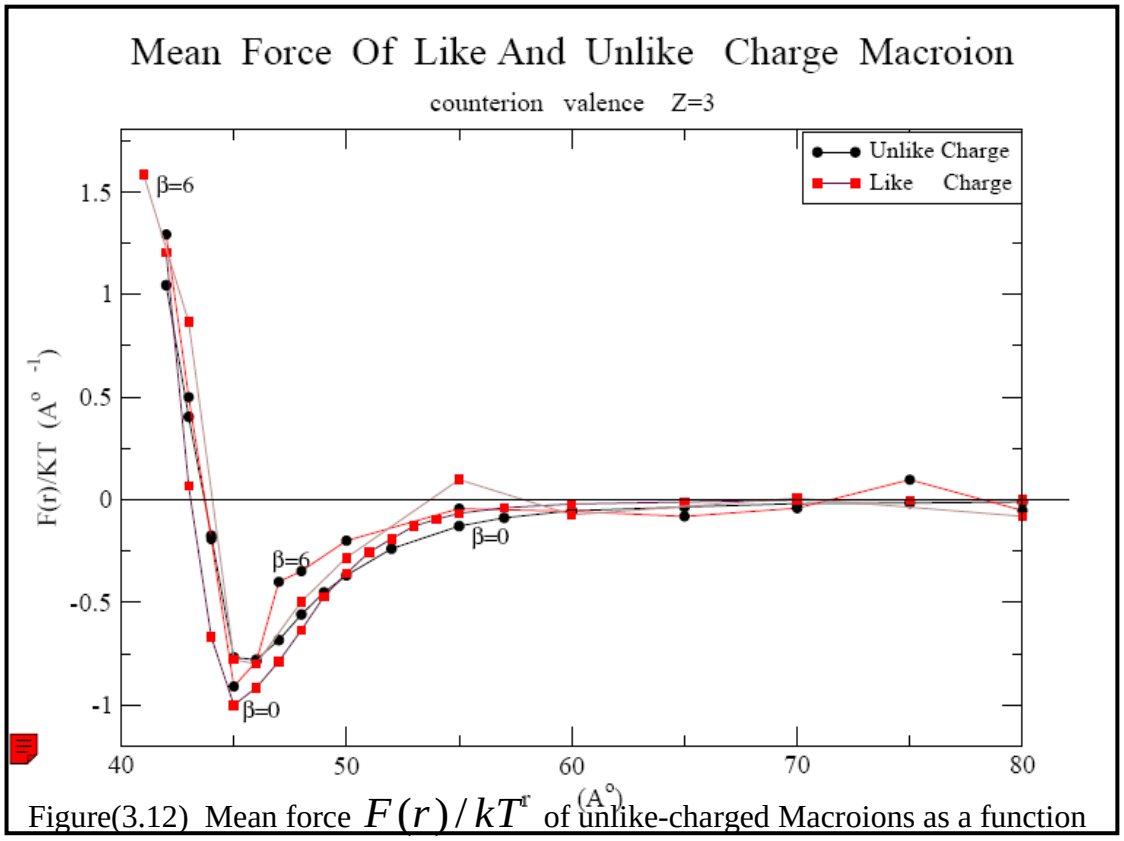
For 60:2 (Zj=2) with amount of added simple 1:3 salt system the mean force is clearly attractive for both like and unlike charged macroion between $44A^{\circ} < r < 52A^{\circ}$, as shown in figure 3.11. For $\beta = 0$ the mean force of unlike charged macroion is less attractive than the mean force of like charged macroion. We note that the mean force at $\beta = 6$ for both like and unlike charged macroions has a maximum value at $r \approx 45A^{\circ}$.



Figure(3.11) Mean Macroion separatio

The attractive mean force of like charged macroions has larger value than unlike charged macroions at $\beta = 6$. Moreover the mean force at $\beta = 6$ is more attractive than the mean force at $\beta = 0$. Finally the magnitude of attractive mean force reduces at $r > 55A^{\circ}$.

The mean force as a function of the macroion separation (r) of like and unlike charge macroions of 60:3 $(Zj = +3)$ asymmetric electrolyte system at $\beta = 0$ and $\beta = 6$ trivalent counterion charge-to-macroion charge ratio of added simple 1:3 salt as shown in figure 3.12 .



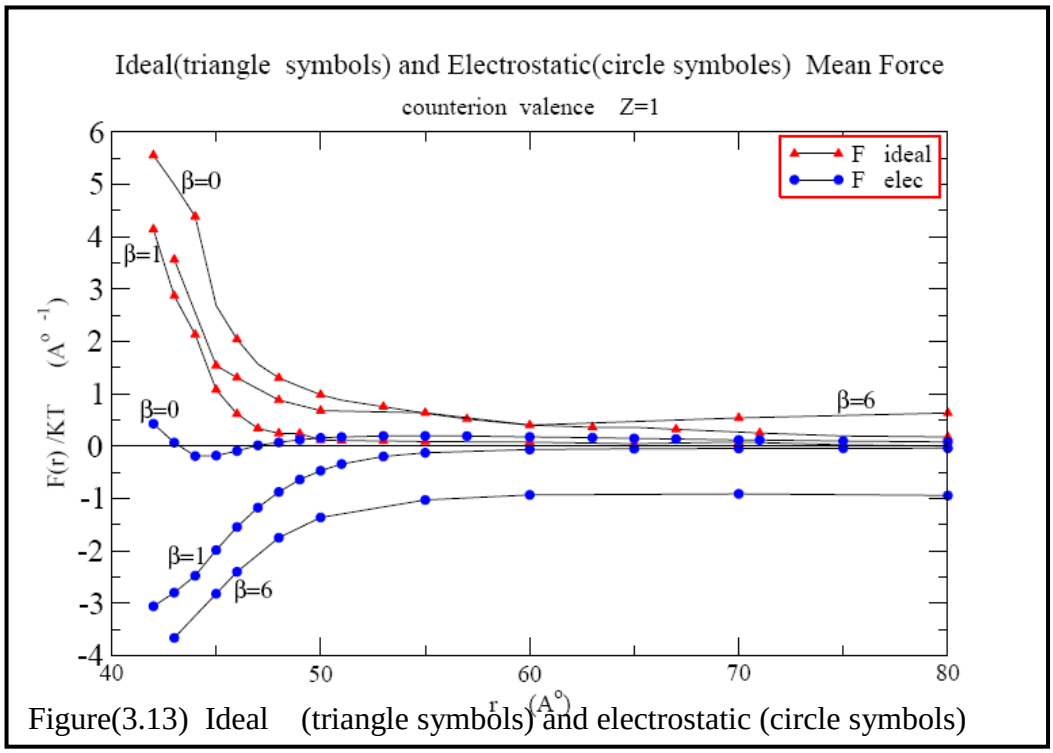
Figure(3.12) Mean force $F(r)/kT^{r}$ of unlike-charged Macroions as a function of Macroion separation r for 60:3 (Z=3) system at $\beta = 0$, and 6.

We note that the repulsive mean force initially decreases especially at short separation, then it becomes attractive, starting at $r = 43A^{\circ}$ and finally the magnitude of the attractive force reduces. Moreover the mean force needs no salt $\beta = 0$ to become attractive. The attractive mean force of like and unlike charged macroions has a maximum value between $44A^{\circ} < r < 55A^{\circ}$ and the maximal attraction appears near $\beta = 0$ of like charged macroion. The mean force of 60:3 at $\beta = 0$ in figure 3.12 resembles that of 60:1 at $\beta = 6$ in figure 3.10 . For like and unlike charged macroions as the valence of counterions (Zj-ions) increase the magnitude of the mean force at $\beta = 0$ and $\beta = 6$ becomes close to each other.

3.3 Force Components

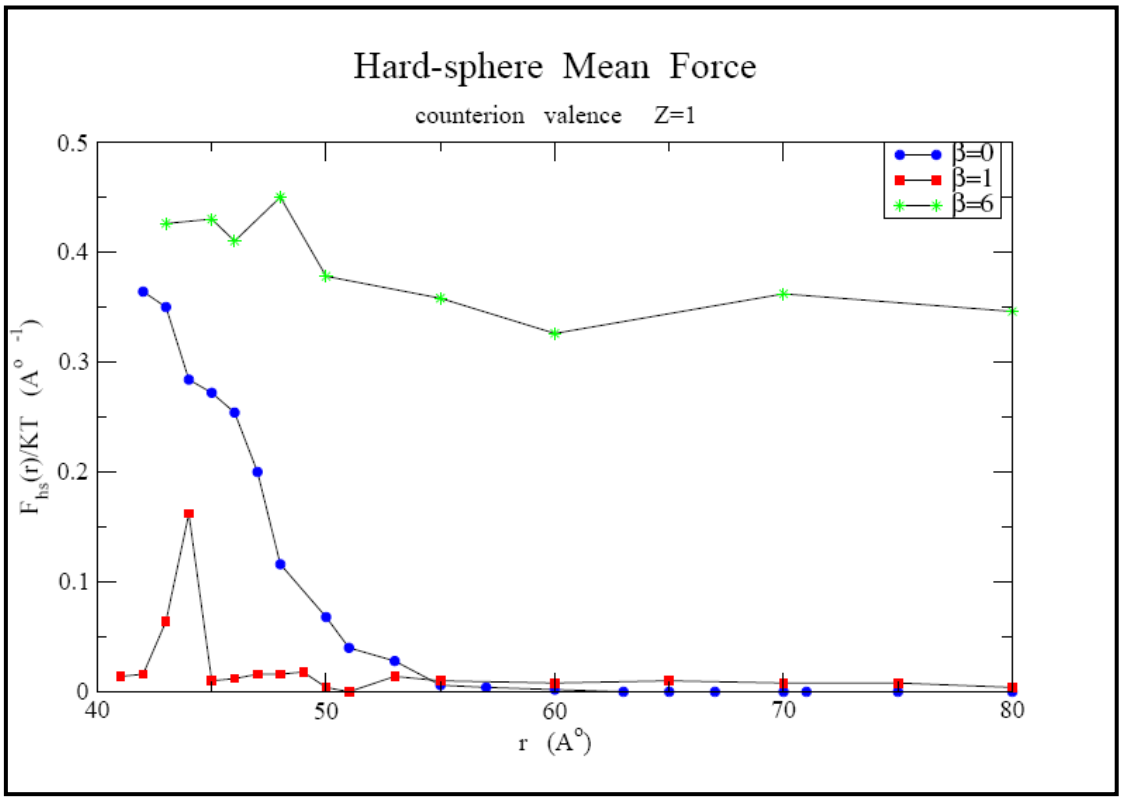
3.3.1 Like Charged Macroions

According to equations 3~ 6 at $\beta = 0,1,and\ 6$ a system of 60:1 (Zj=+1) in a cylindrical cell is considered. Figure 3.13 shows that the ideal component $F_{ideal}(r)$ is repulsive and its magnitude increases montonically as the separation (r) is decreases. Moreover, as the simple 1:3 salt is added, the magnitude of $F_{ideal}(r)$ decreases, displays a minimum at $\beta \approx 1$ and increases at larger amount of salt. Regarding the electrostatic component $F_{elec}(r)$, at $\beta = 0$ it is repulsive at nearly all separations, but becomes purely attractive at $\beta = 1$. At even larger salt concentration $\beta = 6$, the electrostatic contribution becomes continuously more attractive, with the largest attraction appearing at short separation.



Figure(3.13) Ideal (triangle symbols) and electrostatic (circle symbols) contributions to the mean force as a function of the Macroion separation r for 60:1 (Z=1) system at β = 0 ,1 and 6.

The hard-sphere contribution $F_{hs}(r)$ of 60:1 (z=+1) at $\beta = 0,1$ and 6 as a function of the macroion separation (r) is given in figure 3.14. It is always repulsive, but generally small. At $\beta = 0$ it is significant only at short separations. As β is increased $F_{hs}(r)$ is reduced, and at $\beta \approx 1$ it becomes negligible at all separations.

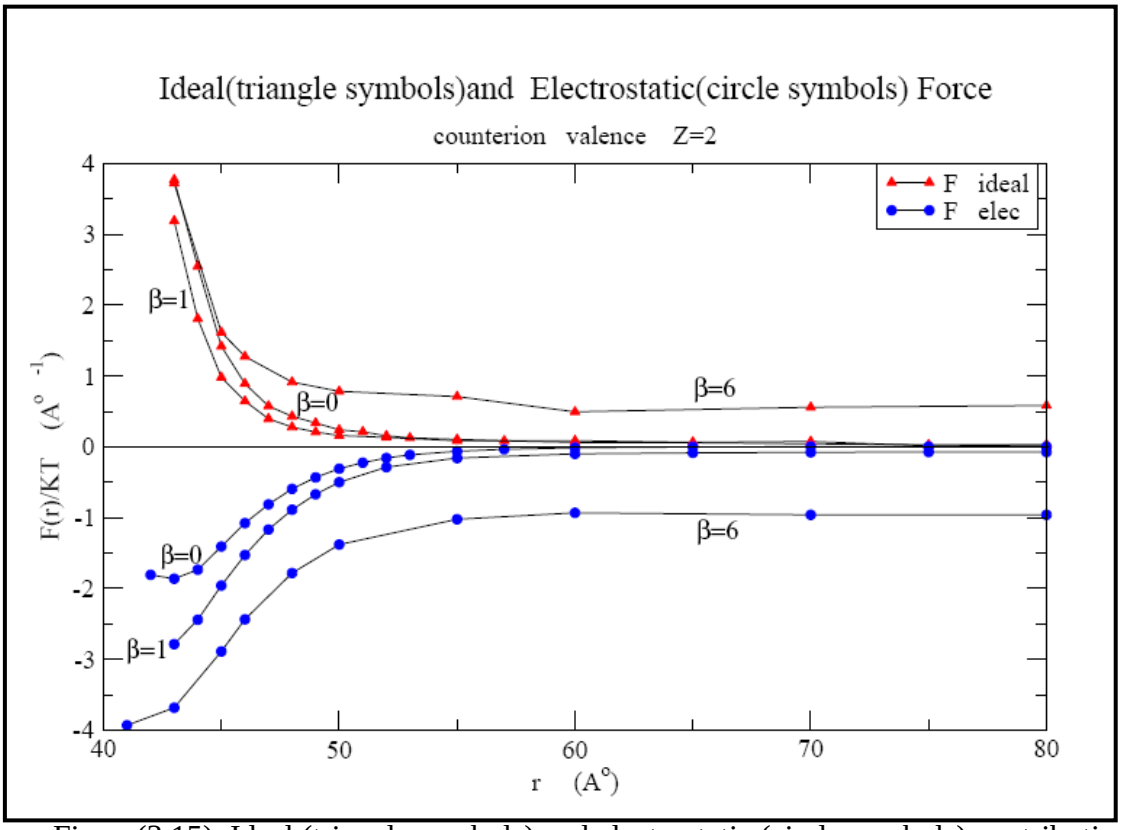


Figure(3.14) Hard-Sphere component to the mean force as a function of the Macroion separation r for 60:1(Z=1) system at β = 0, 1 and 6.

Eventually, at $\beta > 1$ $F_{hs}(r)$ increases in magnitude and becomes only weakly dependent on (r).

The effect of the addition of the simple 1:3 on the mean force components $F_{ideal}(r), F_{elec}(r)$ and $F_{hs}(r)$ is considerable. The ideal component $F_{ideal}(r)$ is repulsive throughout. As the salt is added, $F_{ideal}(r)$ declines rapidly, reaches a minimum at $\beta \approx 1$ and thereafter increases steadily as the separation between macroions (r) decreases. The hard-sphere contribution $F_{hs}(r)$ depends on β in a similar way, i.e. purely repulsive and has a minimum at $\beta = 1$. On the contrary, the electrostatic component $F_{elec}(r)$ decreases continuously as the salt is added. Hence the large repulsive mean force appearing in the salt-free system.

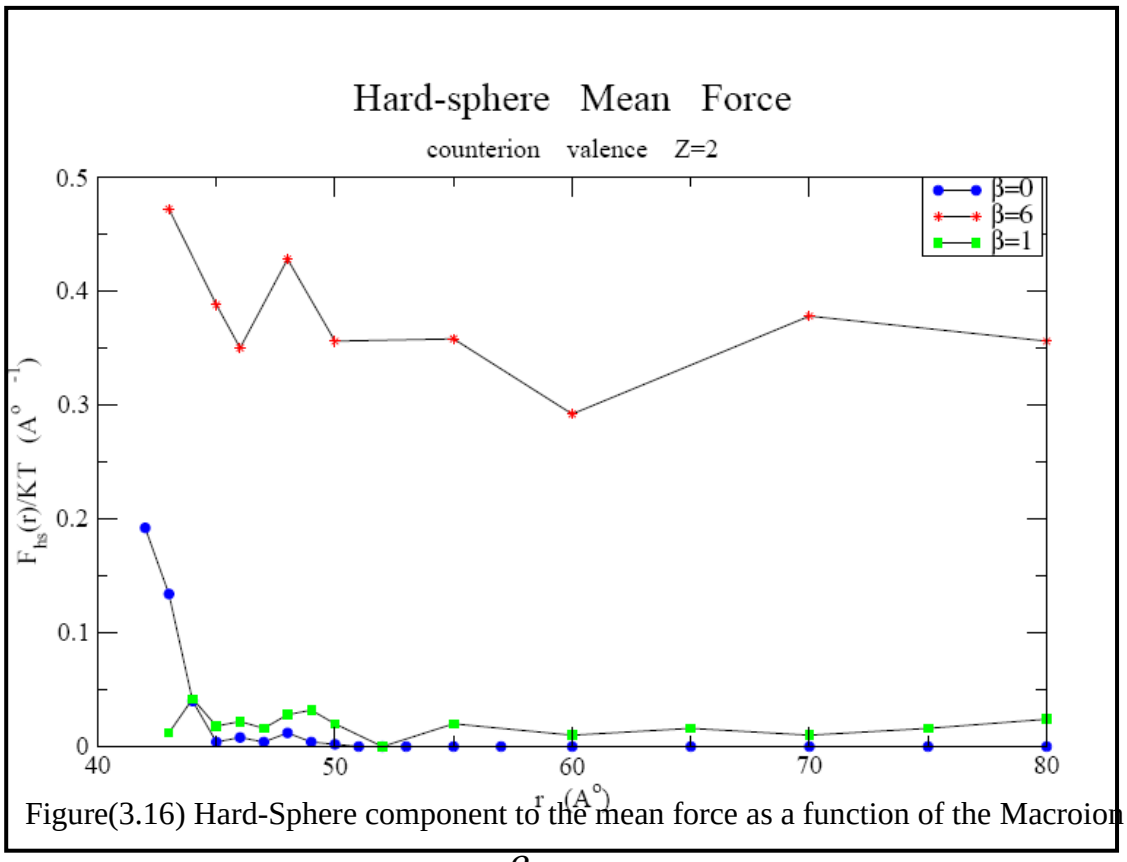
In the case of 60:2 (Zj=+2) asymmetric electrolyte system at various amount of added simple 1:3 salt the components of the mean force at $\beta = 0,1$ and 6 are provided in figure 3.15, We note that the ideal component $F_{ideal}(r)$ is repulsive and its increase as the separation between macroions (r) decreases. Moreover at $\beta = 6$ the ideal component $F_{ideal}(r)$ displays a maximum but decreases displays a minimum at $\beta = 1$.



Figure(3.15) Ideal (triangle symbols) and electrostatic (circle symbols) contributions to the mean force as a function of the Macroion separation r for 60:2 (Z=2) system at β = 0, 1 and 6.

Regarding the electrostatic component $F_{elec}(r)$, at $\beta = 0$, it is obviously attractive at short separations $r < 55A^{\circ}$ while it is repulsive in 60:1 system as shown in figure (3.13) . It becomes purely attractive at $\beta = 1$. At even larger salt concentration, $\beta = 6$, the electrostatic contribution becomes continuously more attractive with the largest attraction appearing at short separation.

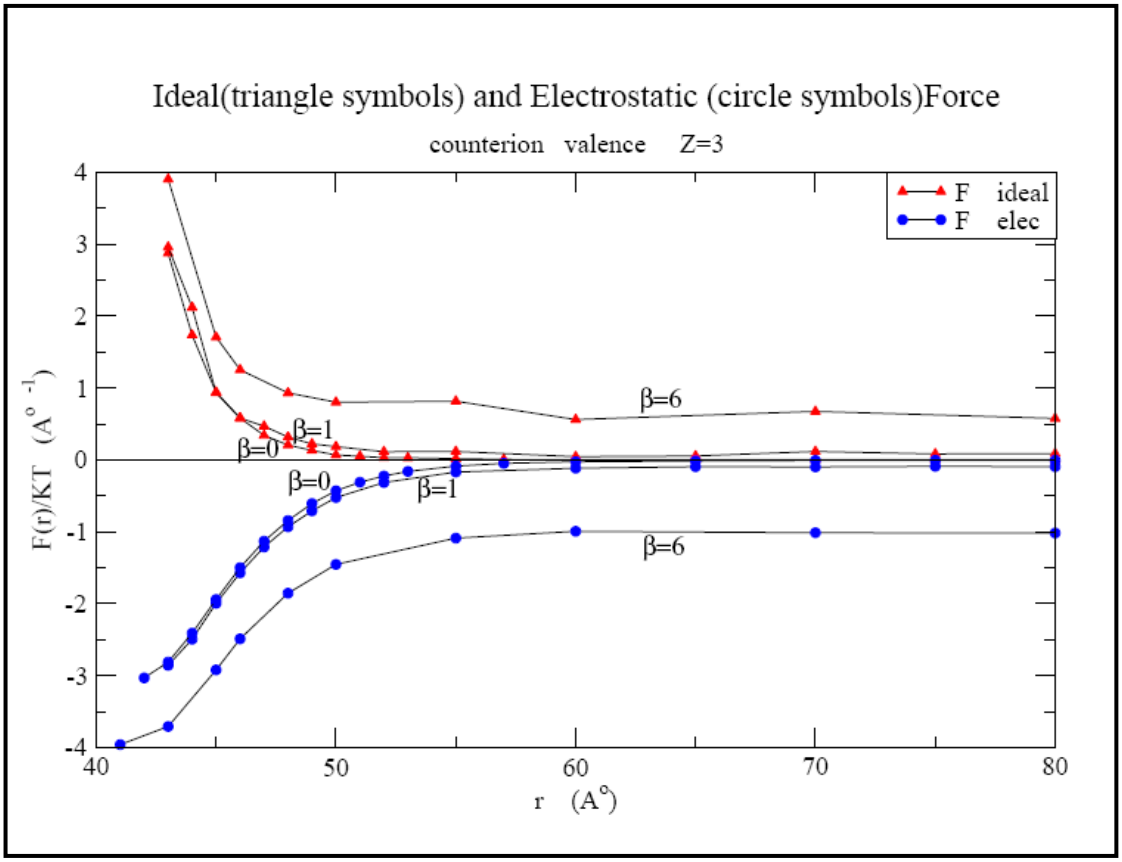
The hard-sphere component $F_{hs}(r)$ contribution is given in figure 3.16, in 60:2 (Zj=+2) system. It is still always repulsive as in previous 60:1 (Zj=+1) system. At $\beta = 0$ we note it becomes more attractive starting at $r \approx 44A^{\circ}$, it has a maximum value at $r = 45A^{\circ}$.



Figure(3.16) Hard-Sphere component to the mean force as a function of the Macroion separation r for 60:2(Z=2) system at β = 0, 1 and 6.

At $\beta = 6$ $F_{hs}(r)$ increases in magnitude and becomes only weakly dependent on (r). The hard- sphere contribution $F_{hs}(r)$ depends on β. It is repulsive and a minimum at $\beta = 0$.

On the other hand the ideal $F_{ideal}(r)$ and the electrostatic $F_{elec}(r)$ components of the mean force in 60:3 (Zj=+3) asymmetric electrolyte system at various amount of added simple 1:3 salt is considered figure 3.17 . We also note that as in 60:1 and 60:2 system the ideal components $F_{ideal}(r)$ is repulsive and its magnitude increases as the separation between macroions r is decreases. We can see that at the magnitude of $F_{ideal}(r)$ has a maximum at $\beta = 6$, and decreases at small amount of salt.

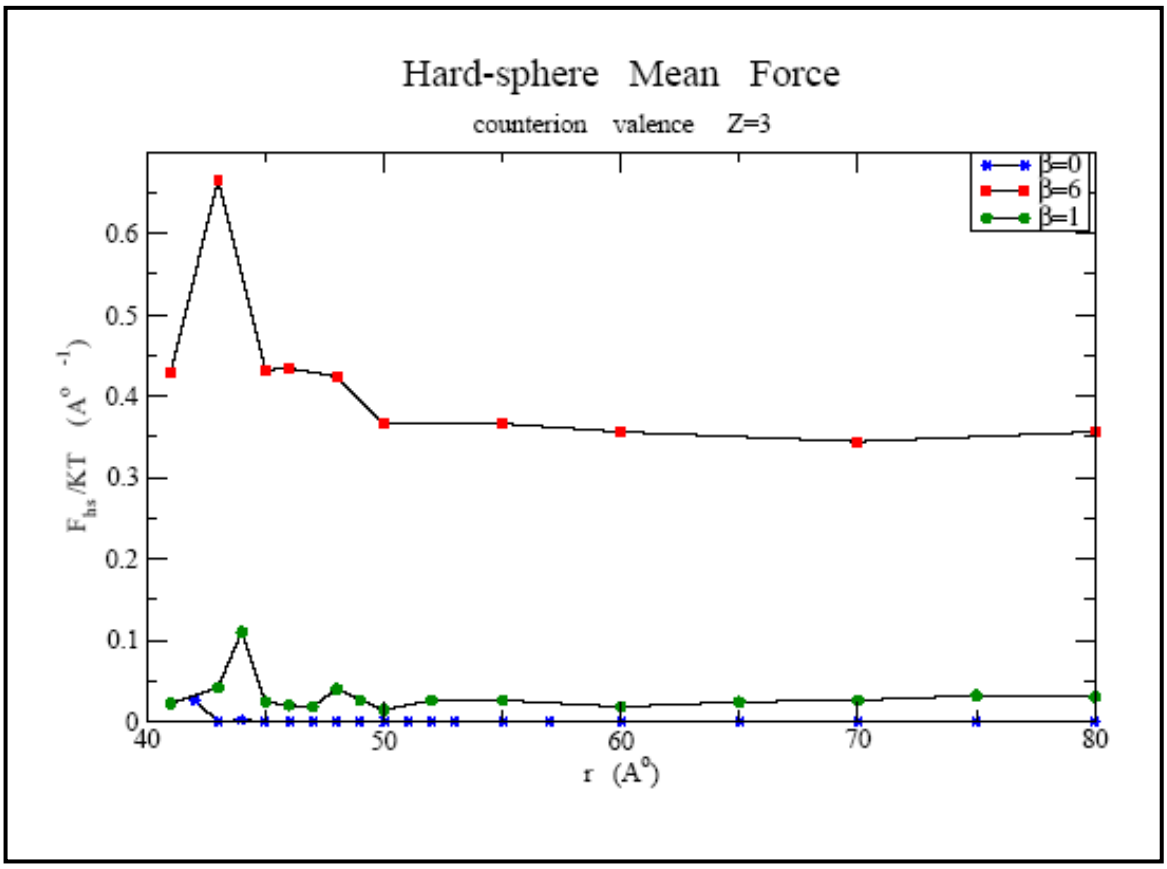


Figure(3.17) Ideal (triangle symbols) and electrostatic (circle symbols) contributions to the mean force as a function of the Macroion separation r for 60:3 (Z=3) system at β = 0, 1 and 6.

The ideal component $F_{ideal}(r)$ displays a minimum at $\beta = 0$. For the electrostatic component $F_{elec}(r)$, it is attractive at $\beta = 0$,1,6 for all separations (r), but it becomes more attractive at $\beta = 1$, with the layer set attraction appearing at short separation.

The hard-sphere contribution $F_{hs}(r)$, given in figure 3.18, is always repulsive.

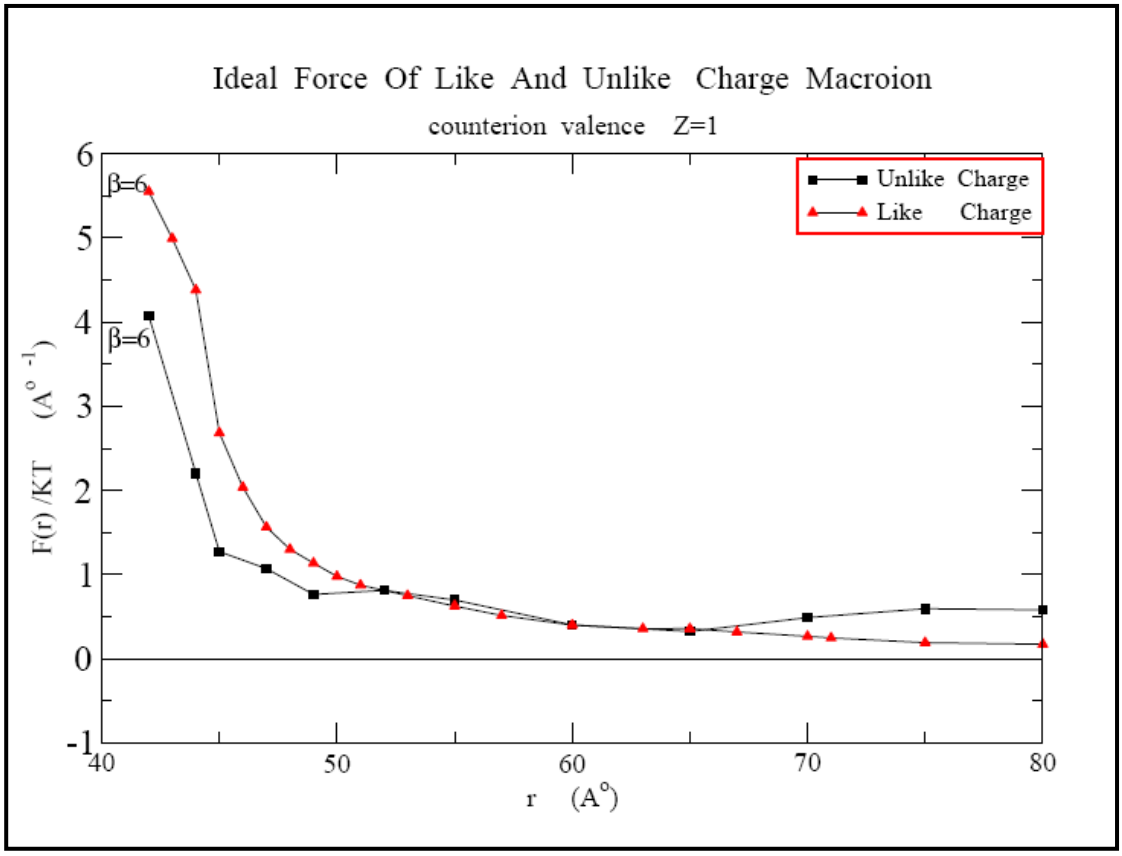
We have noted that at $\beta = 0$ it becomes negligible at all separators. Moreover as β is increased $F_{hs}(r)$ is increased. The magnitude of $F_{hs}(r)$ depends on β and has a maximum at $\beta = 6$. We have seen that at $\beta = 1$ and 6, $F_{hs}(r)$ displays a maximum at macroions separations $r \approx 43A^{\circ}$.



3.3.2 Unlike Charged Macroions

Let us now consider the 60:1 $(Z_j = +1)$ asymmetric electrolyte system at various amount of added simple 1:3 salt, where the trivalent ions are of opposite charge to the unlike

charged macroions. Two different charged macroions (-30) and (-90) exist in the cylindrical cell. The ideal force $F_{ideal}(r)$ of like and unlike charged macroions of $\beta = 6$ as a function of a macroion separation (r) is shown in figure 3.19 . $F_{ideal}(r)$ is repulsive and its magnitude increases as the separation (r) is decreased. Moreover it declines rapidly for unlike charged macroions more than like charged macroions at $r < 50A^{\circ}$.

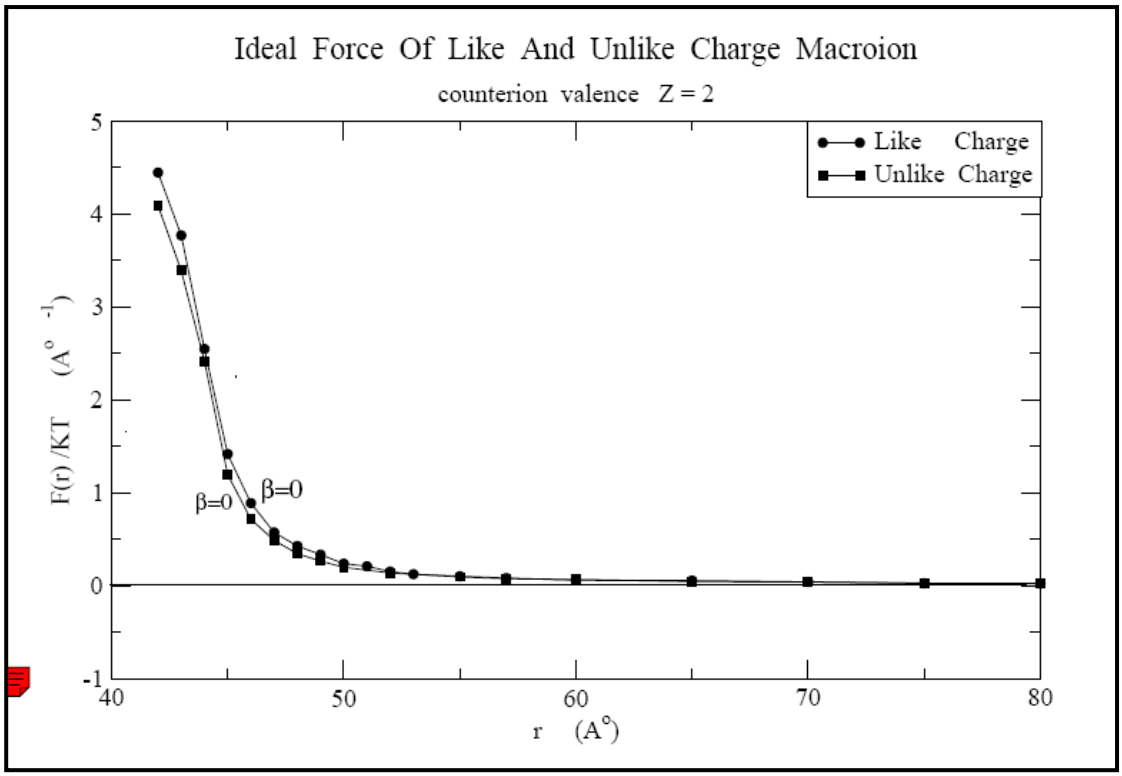


Figure(3.19) Ideal for

At $r > 50A^{\circ}$, they are still repulsive and nearly equal but the magnitude of $F_{ideal}(r)$ of unlike charged macroions becomes more at long separation (r separation r of the lik).

If now consider 60:2 $(Z_j = +2)$ system but without salt $\beta = 0$. Figure 3.20 shows the ideal force $F_{ideal}(r)$ of the like and unlike charged macroions at $\beta = 0$ $F_{ideal}(r)$ still repulsive as in 60:1 $(Z_j = +1)$ system and its magnitude decreases as the separations between macroions (r) is increases. We have noted that the magnitude of $F_{ideal}(r)$ for like

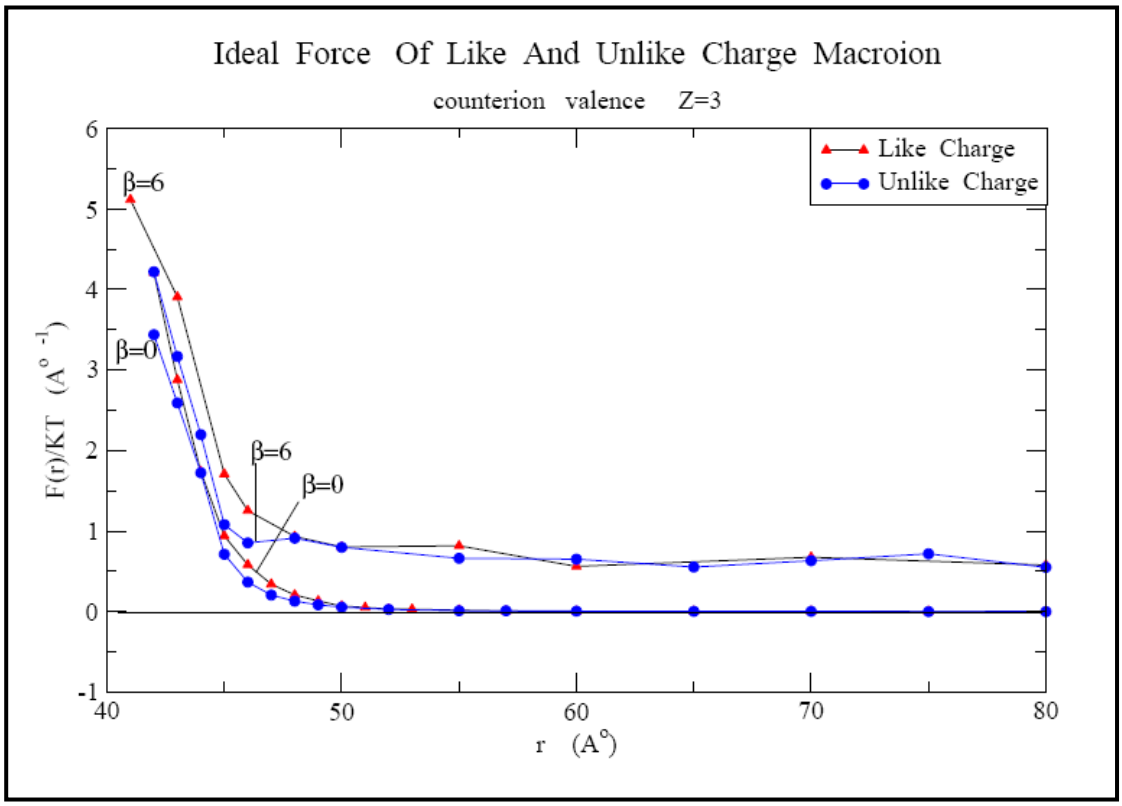
charged macroions is slightly greater than for unlike charged macroions between $45A^{\circ} < r < 50A^{\circ}$ and they become nearly equals and negligible at $r > 50A^{\circ}$.



Figure(3.20) Ideal f

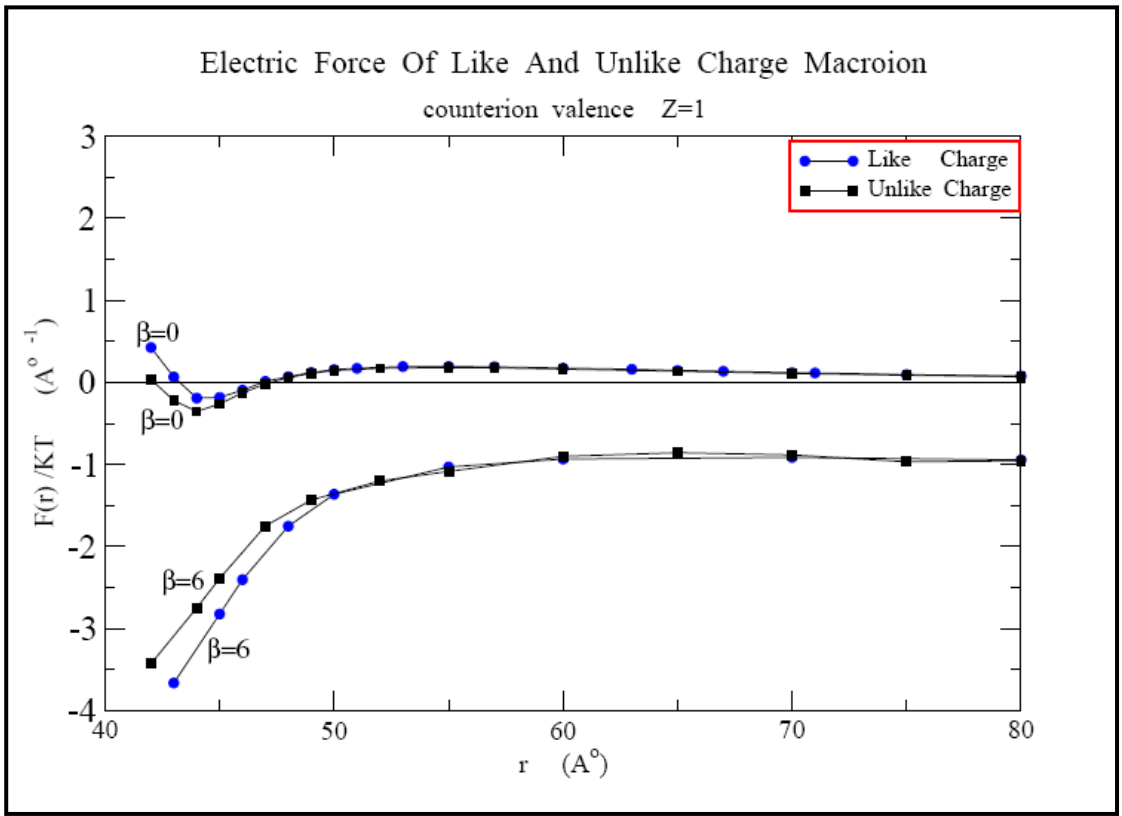
In the case of 60:3 $(Z_j = +3)$ system, the ideal component $F_{ideal}(r)$ of the mean force at $\beta = 0$ and $\beta = 6$ for both like and unlike charged macroions are shown in figure 3.21. We note that as salt added $\beta = 6$ the ideal force become more repulsive for both like and unlike charged macroions. The ideal $F_{ideal}(r)$ component is always repulsive for both like and unlike charged macroions and for $\beta = 0$ and $\beta = 6$ values. There is no difference between like and unlike systems on ideal component of the mean force.

separation r of the l



I f now consi der the syste m 60:1 $(Z_j = +1)$ asym metri c electrolyte system, electrostatic components $F_{elec}(r)$ of the mean force at $\beta = 0$ and $\beta = 6$ in the case of like and unlike charged macroions at $\beta = 0$ and 6 shown in figure 3.22 .

Figure(3.21) Ideal f separation r of the l



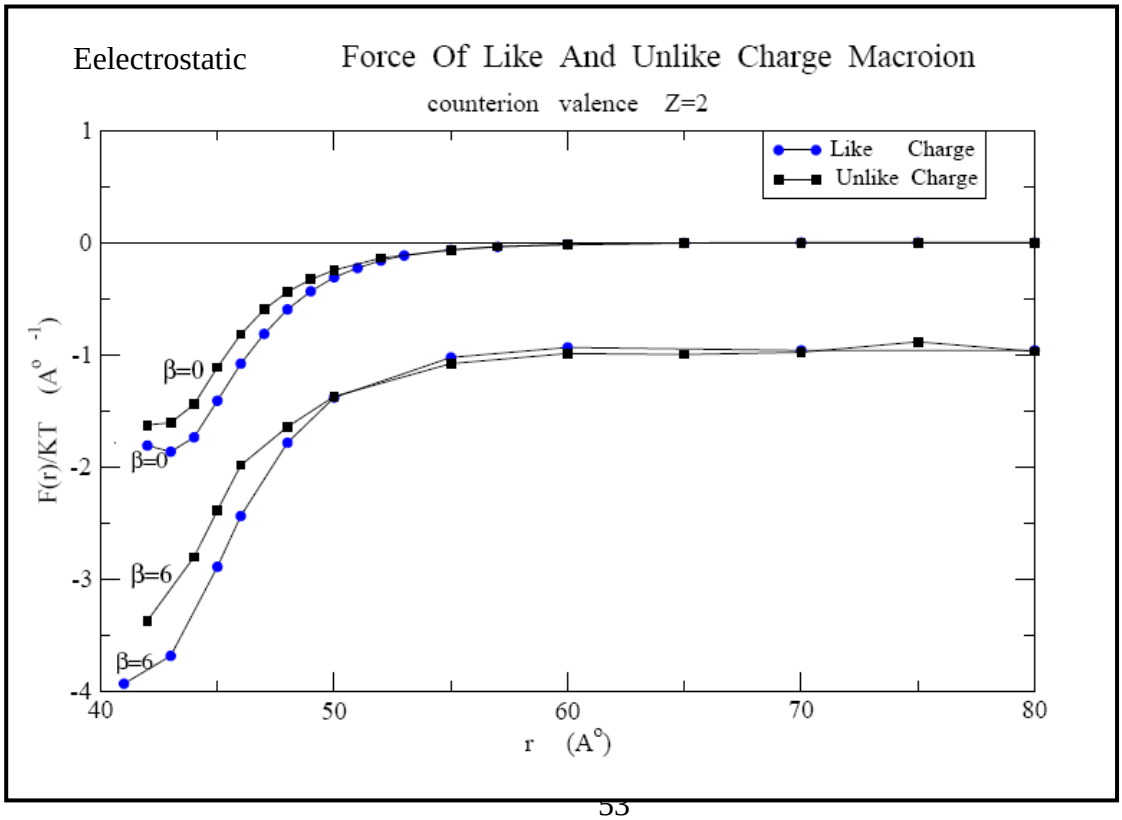
Eelectrostatic

W e not that $F_{elec}(r)$ at $\beta = 0$ for

like and unlike charged macroions is repulsive at nearly all separations, except between $43A^{\circ} < r < 48A^{\circ}$, it is attractive. At large salt concentration $\beta = 6$, the electrostatic contribution $F_{elec}(r)$ becomes attractive for like and unlike charged macroions. Moreover it is more attractive for like charged than unlike charged macroions at $\beta = 6$ at short separations. Hence, the large repulsive electrostatic contribution force $F_{elec}(r)$ appearing in the salt free system i.e. at $\beta = 0$.

In the case of 60:2 $(Z_j = +2)$ system the electrostatic components $F_{elec}(r)$ in the case of like and unlike charged macroions at $\beta = 0$ and $\beta = 6$ is shown in figure 3.23. It is purely attractive at short separations, but it becomes negligible at $r < 55A^{\circ}$ for $\beta = 0$. We note that $F_{elec}(r)$ for 60:2 is more attractive than 60:1. Moreover as β is increased, $\beta = 6$, the electrostatic component becomes more attractive with the largest attraction appearing at short separation.

More attractive we also note that $F_{elec}(r)$ is more attractive in the case of like charged macroions.



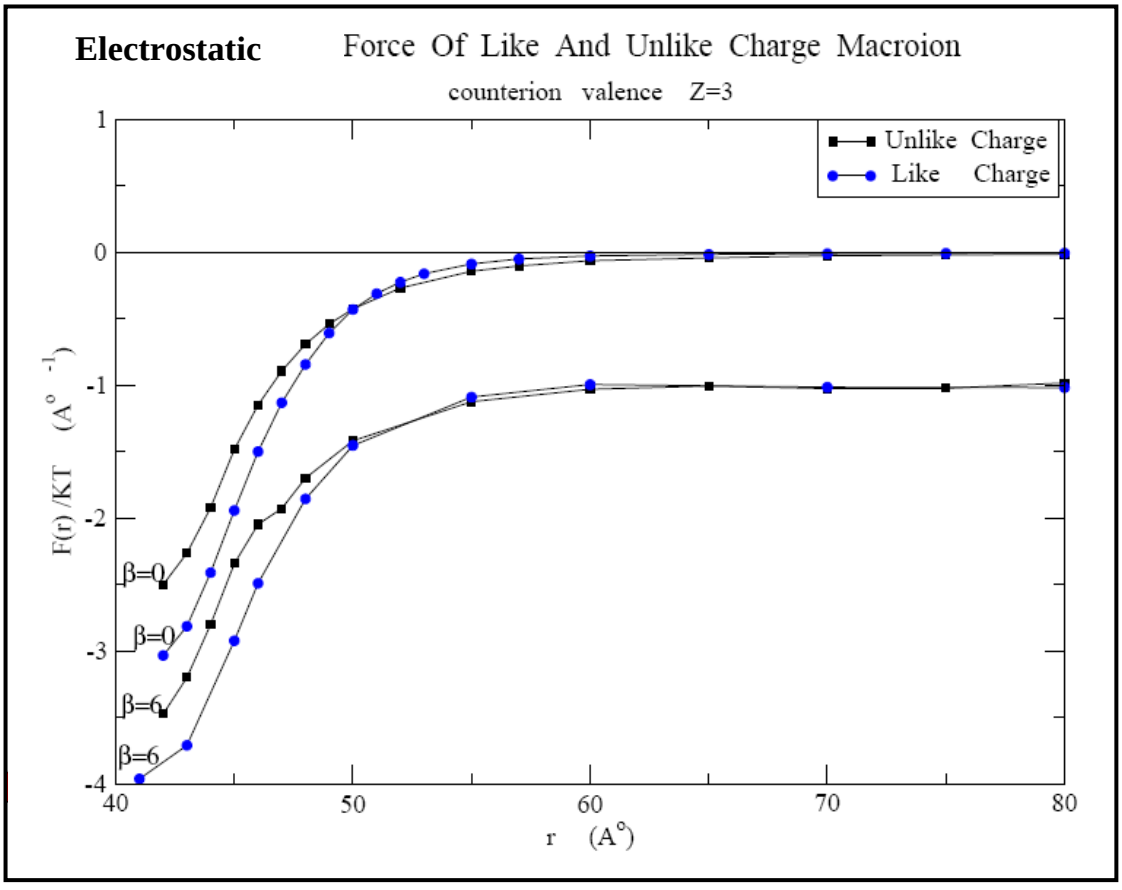
Figure(3.23) Elec

separation r of lik

If now consider the 60:3 $(Z_j = +3)$ system at

$\beta = 0$ and $\beta = 6$.

The electrostatic component of the mean force in the like and unlike charged macroions is given in fig 3.24. We note that $F_{elec}(r)$ is attractive in salt free system $\beta = 0$ and salt added system $\beta = 6$ but it becomes also, like 60:2 system, negligible at $\beta = 0$ at long separations $r > 60A^{\circ}$. But the attraction is more at $\beta = 6$ than at $\beta = 0$, with the largest attraction appearing at short separations.

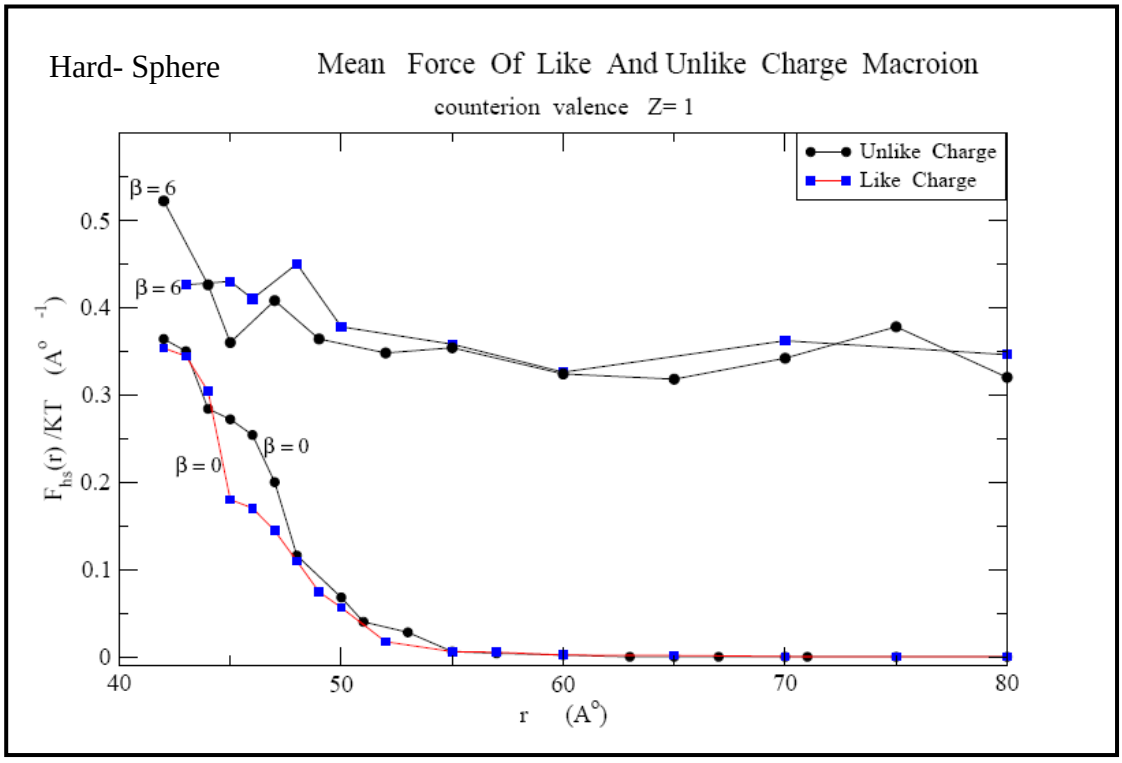


Figure(3.24) Electrostatic force component of the mean force as a function of Macroion separation r of like and unlike charged Macroions for 60:3 (Z=3) system at β =0 and 6

The magnitude of $F_{elec}(r)$ of like charged is more than of unlike charged macroions.

The Hard-Sphere contribution $F_{hs}(r)$ as a function of macroions separations (r) in 60:1 $(Z_j = +1)$ system of like and unlike charged macroions is given in figure 3.25. It is always repulsive at $\beta = 0$ and $\beta = 6$, but generally small. At $\beta = 0$ it is significant only at short separations. At large amount of salt $\beta = 6$ $F_{hs}(r)$ increase in magnitude and becomes only weakly dependent on (r).

We note that the $F_{hs}(r)$ in the case of like charged macroions is more repulsive than unlike charged macroions at $\beta = 6$ between $45A^{\circ} < r < 55A^{\circ}$.



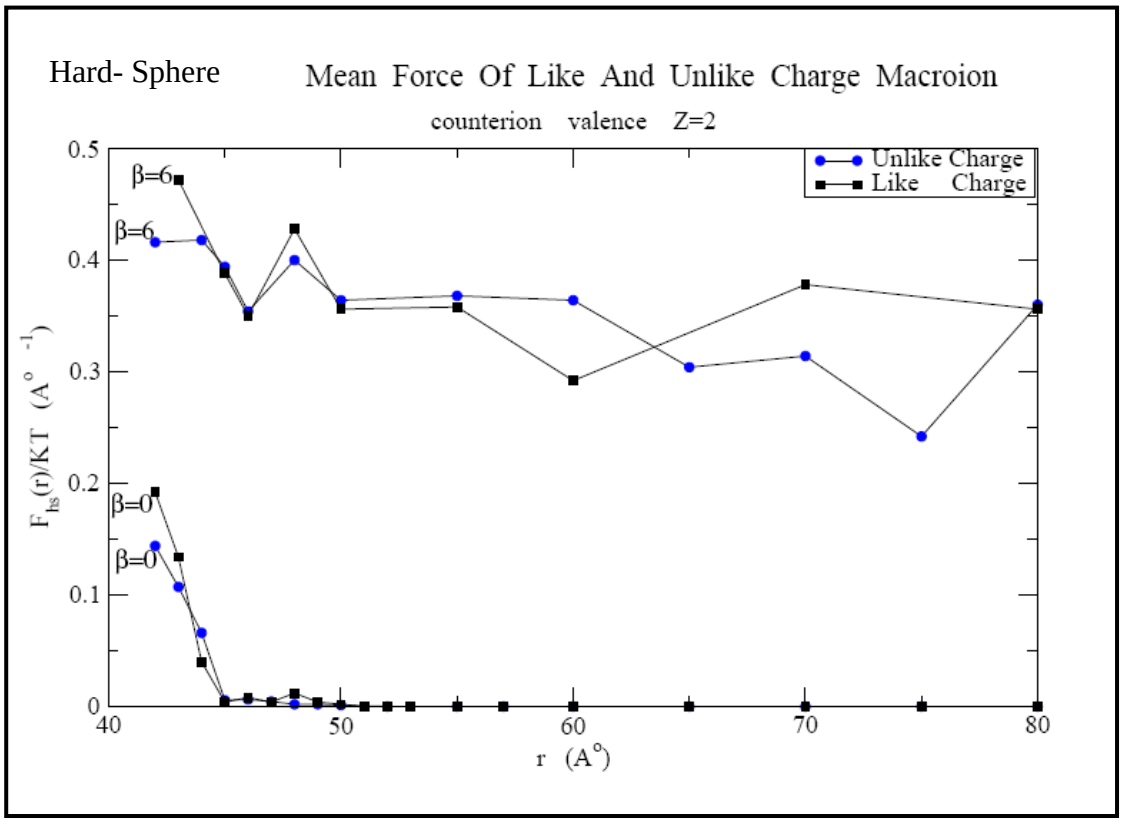
Figure(3.25) Hard-S

At $\beta = 0$ $F_{hs}(r)$ is less repulsive for like charged between $45A^{\circ} < r < 50A^{\circ}$, at $r > 50A^{\circ}$ it becomes negligible for like and unlike charged macroions.

separation r of like

The hard-sphere contributions $F_{hs}(r)$ of the mean force of like and unlike charged macroions for 60:2 $(Z_j = +2)$ as a function of macroions separation (r) is shown in figure 3.26, we note that it is always repulsive, but generally small similar to 60:1 system. At $\beta = 0$ it declines rapidly and becomes negligible at $r > 45A^\circ$. Moreover at $\beta = 6$ it has a maximum value at $r \approx 43A^\circ$.

It is more repulsive for like charged macroions system between $48A^\circ < r < 50A^\circ$, but it reversed between $50A^\circ < r < 64A^\circ$, and it also reversed again at $r > 64A^\circ$.

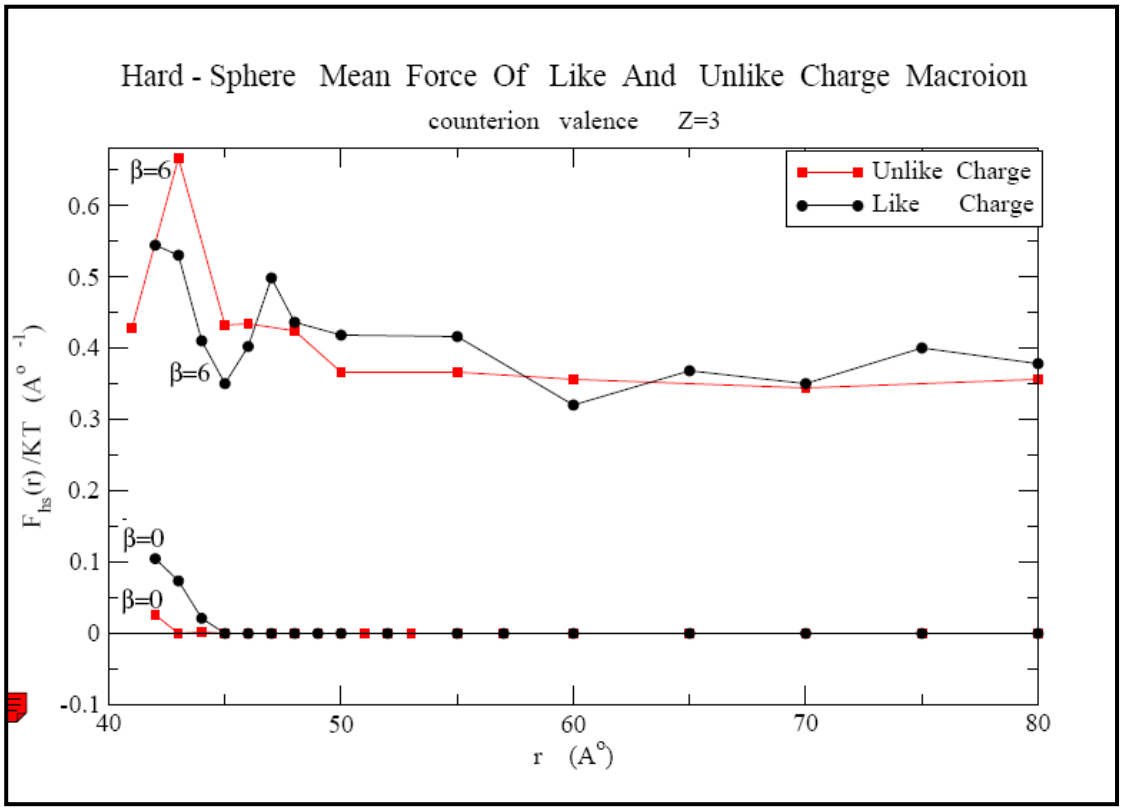


Figure(3.26) Hard-S

We have noted the alternating of $F_{hs}(r)$ in like and unlike charged macroions at $\beta = 6$.

separation r of like

If now 60:3 $(Z_j = +3)$ system is considered, the hard-sphere contribution $F_{hs}(r)$ as a function of macroions separation (r) of like and unlike charged macroions is shown in figure 3.27 .



Figure(3.27) Hard-S

It is always repulsive as in 60:1 and 60:2 systems. Its magnitude becomes less repulsive specially at $\beta = 0$ at short separations comparison by separation r of like

60:1 and 60:2 systems. Moreover it becomes more repulsive for like charged macroions at $r > 45A^{\circ}$ it becomes negligible. For $\beta = 6$ the $F_{hs}(r)$ of unlike charged macroions is more repulsive and has a maximum at $r \approx 44A^{\circ}$, then it reversed between $46A^{\circ} < r < 68A^{\circ}$. Finally the $F_{hs}(r)$ is weakly dependent on (r) at $\beta = 6$.

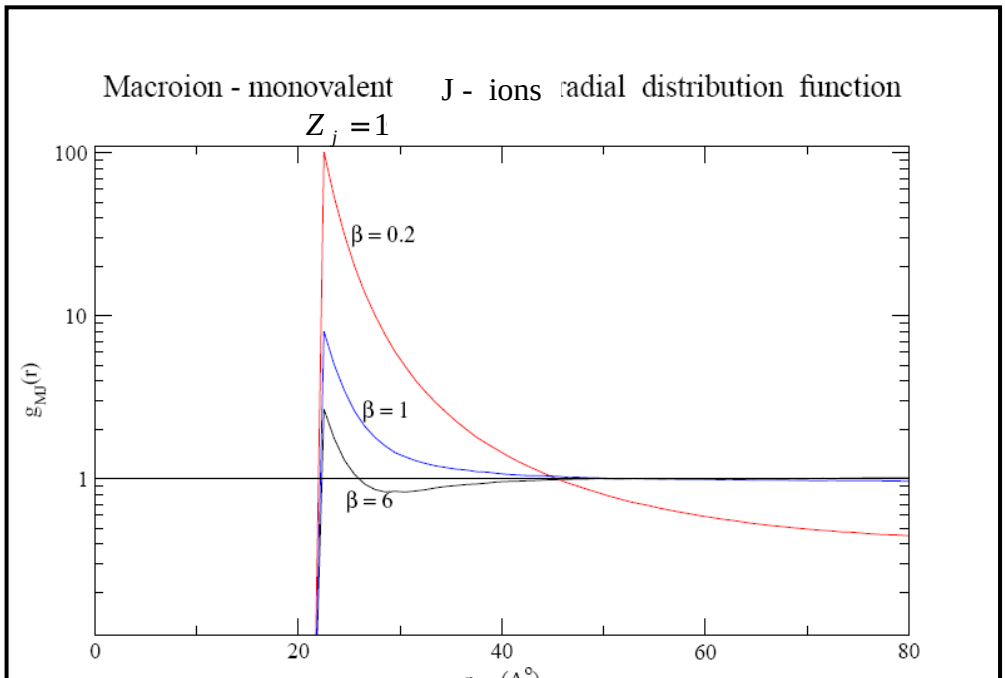
We note that the addition of 1:3 salt (I-ions) makes the hard-sphere component more repulsive as shown in figure 3.27 .

3.4 Radial Distribution Functions

The distribution of the small ions near a macroion has been examined by determination of macroion-small ion radial distribution function (rdfs) providing the relative densities of small ions at distance r from the macroions, its value being unity in the absence of any spatial correlation. In this analysis, a spherical cell containing one macroion and appropriate number of small ions has been employed. The three macroion-small ion (rdfs) in 60:1, 60:2, and 60:3 systems at trivalent counterion charge – to – macroion charge ratio $\beta = 0.2\ ,1\ ,and\ 6$ will be discussed.

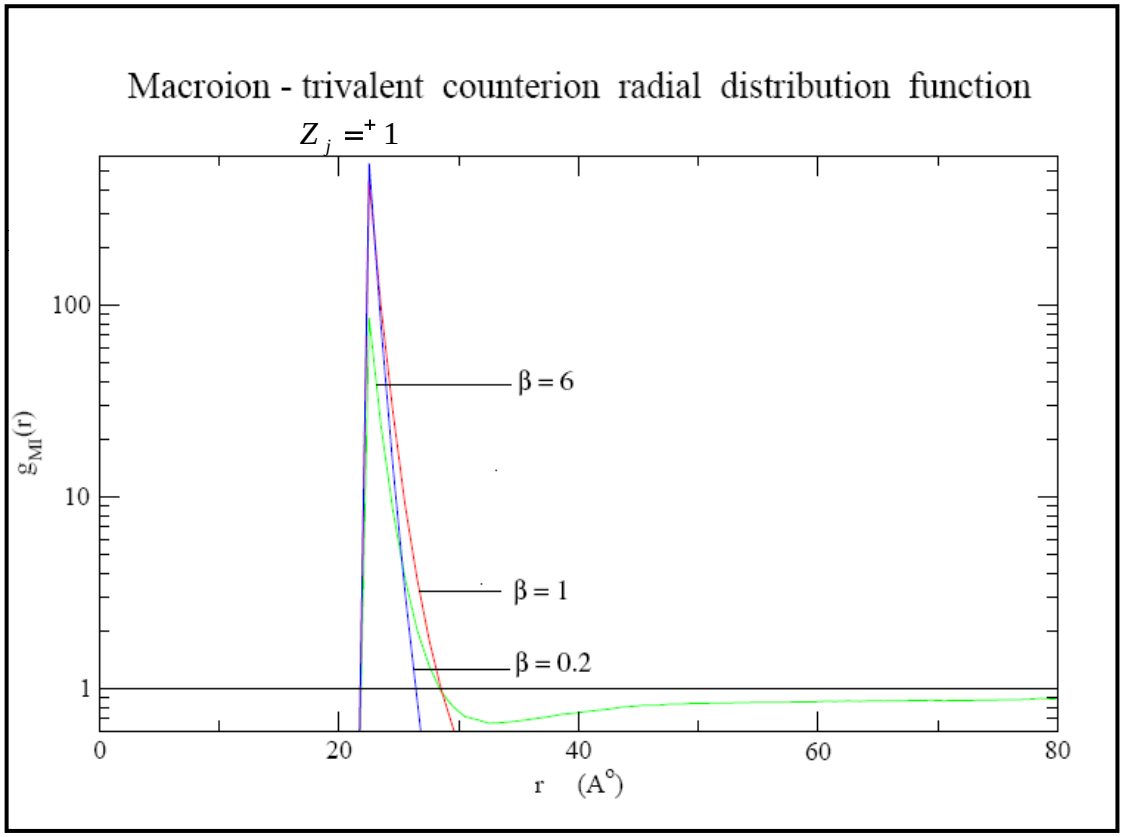
3.4.1 60:1 $(Z_i = +1)$ *system*

The macroion-monovalent counterion (J-ion) (rdfs) $g_{MJ}(r)$ displayed in figure 3.28 have maxima at the hard-sphere contact separation $r = R_M + R_J = 22A^\circ$ clearly demonstrating the accumulation of the counterions near the macroions. At $\beta = 0.2$, the contact value is ≈ 100 implying that the counterion density at the macroion surface is 100-fold layer than the average counter density. As more salt is added the contact value decreases monotonously and amount to 8 at $\beta = 1$, and about to 4 at $\beta = 6$.



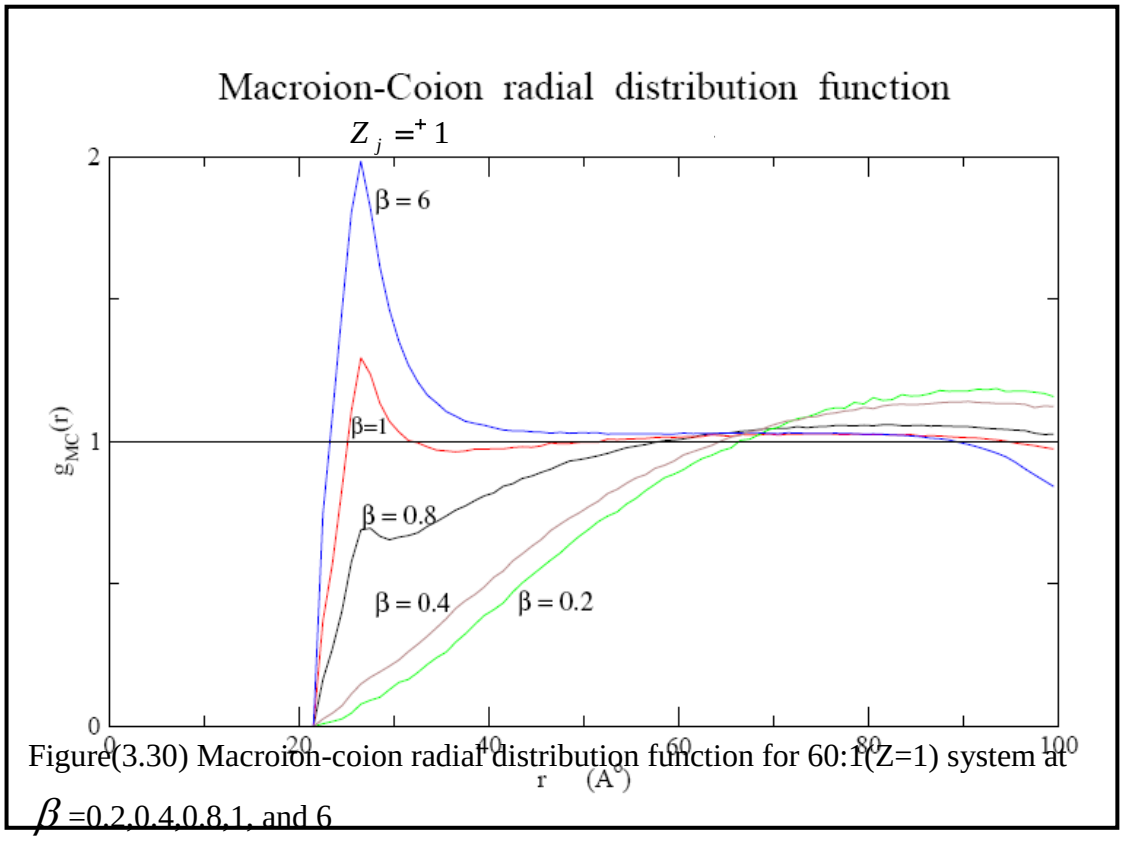
Figure(3.28) Macroions-monovalent counterion radial distribution function for 60:1 (Z=1) system at β =0,0.2,1 and 6

The strong accumulation of the trivalent counterions (I-ions) near the macroions is quantified in figure 3.29 . At small β, the macroion-trivalent counterion (rdf) demonstrates the essentially quantitative accumulation of these ions. At further addition of salt, the contact values decrease, but with large excess of salt $\beta = 6$ the radial distribution function approaches unity at large separation. We also notice that at $\beta = 1$, the contact value of the macroion-trivalent counterion (rdf) is ≈ 400 as compared to ≈ 8, for macroion- monovalent counterion rdf, quantifying the much stronger preference of the trivalent to be near the macroion.



Figure(3.29) Macroions-trivalent counterion radial distribution function for 60:1 (Z=1) system at β =0,0.2,1 and 6

The macroion-coion radial distribution function $g_{MC}(r)$ given in figure 3.30. It shows that the coions are expelled from the macroions vicinity at low salt concentration and that this effect becomes less pronounced upon addition of salt. At $\beta = 1$ the coions are uniformly distributed except for an enhanced local density about $r \approx 26A^{\circ}$ and reduced local density at macroion contact. The location of the maximum corresponds to a separation from the macroion surface sufficient to accommodate a monolayer of counterions in between. The largest accumulation of coions is at $\beta = 6$.

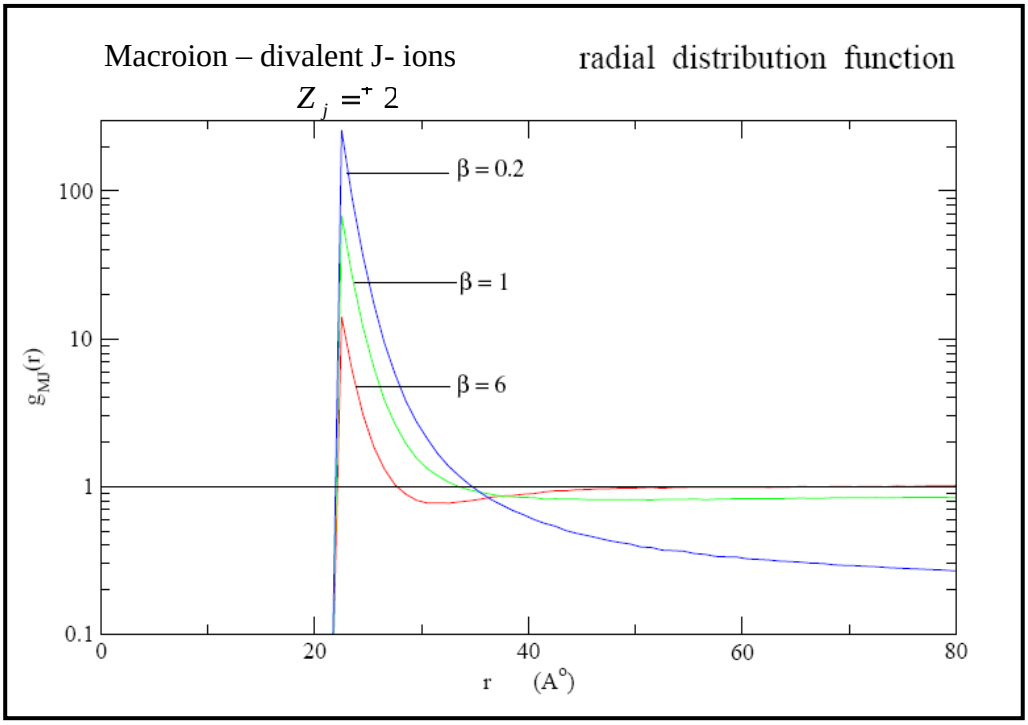


Figure(3.30) Macroion-coion radial distribution function for 60:1(Z=1) system at β =0.2,0.4,0.8,1, and 6

3.4.2 60:2 $(Z_j = +2)$ system

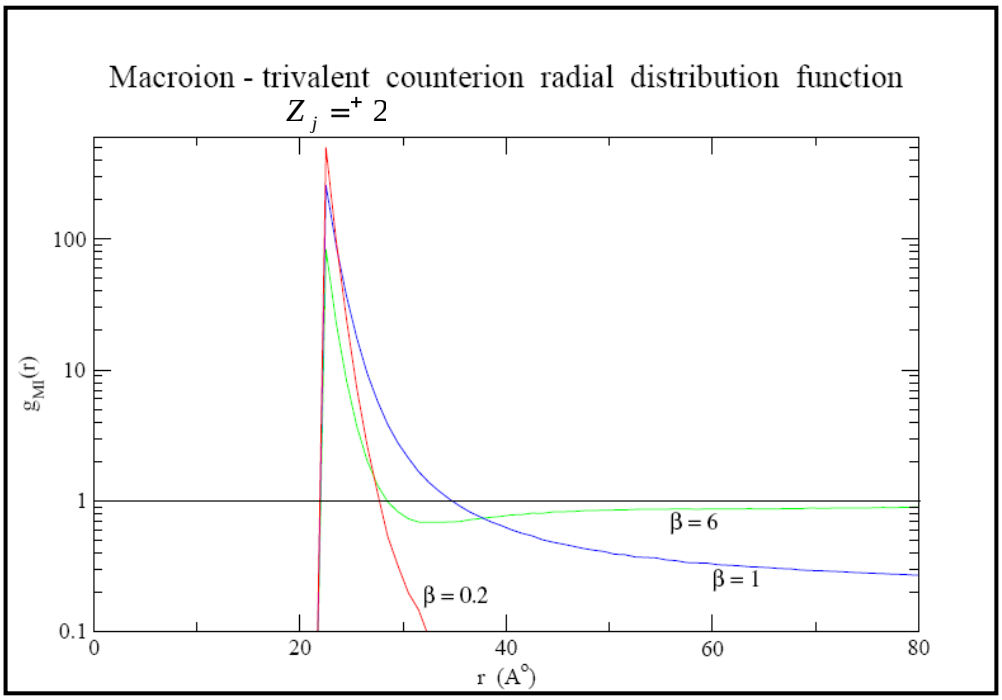
Let us now consider the 60:2 $(Z_j = +2)$ at various amount of added simple 1:3 salt, $\beta = 0.2$,1 and 6, will be employed. The macroion – monovalent counterion (I-ions) radial distribution function $g_{MC}(r)$ is shown in figure 3.31 .

They have maxima at the hard-sphere contact separation $r = R_M + R_J \approx 22A^\circ$ similar to 60:1 $(Z_j = +1)$ system. At $\beta = 0.2$, the contact value is ≈ 200, more than 60:1 $(Z_j = +1)$ system, implying that the counterion density of the surface is 200-fold larger than the average counterion density. As more salt is added, the contact value decrease and amounts to 100 and 10 at $\beta = 1$, $\beta = 6$ respectively.



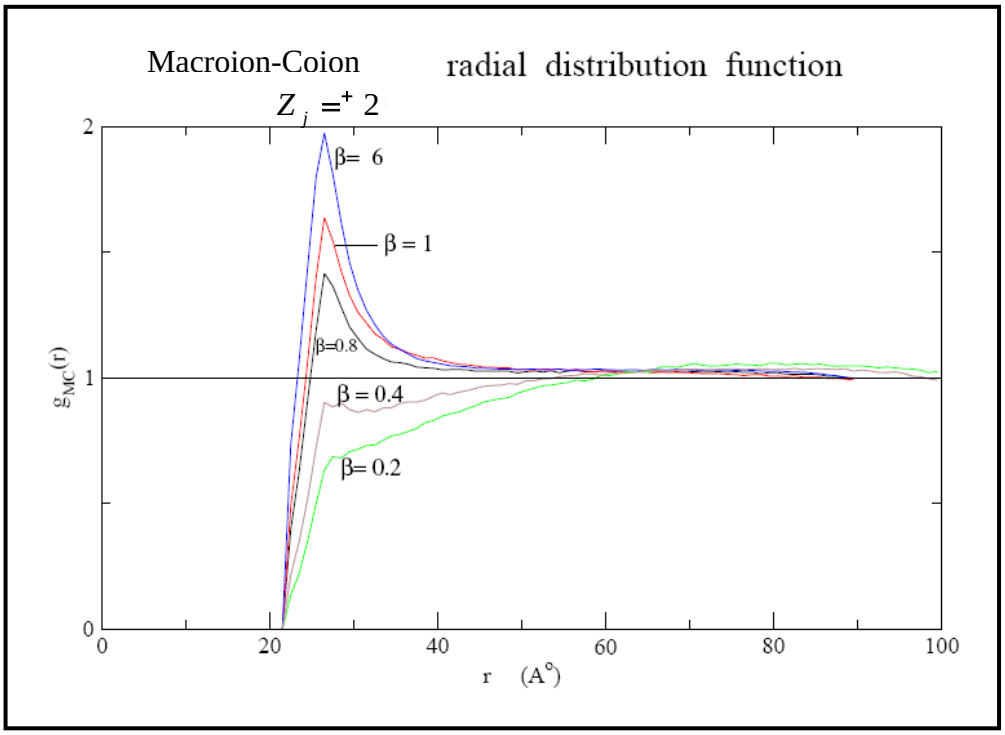
Figure(3.31) Macroions-monovalent counterion radial distribution function for 60:2 (Z=2) system at β =0,0.2,1 and 6

We can note the accumulation of the trivalent counterions (I-ions) near the macroions is stronger than of monovalent counterions (j-ions) as shown in figure 3.32. At $\beta = 0.2$ the macroion-trivalent counterion rdf demonstrates the essentially quantitative accumulation of (I-ions), the contact value is ≈ 800. At $\beta = 1$ and $\beta = 6$, the distribution becomes more even, but the radial distribution function approaches unity at large separation first with large excess of salt. At $\beta = 1$, the contact value of $g_{MI(r)}$ rdf is ≈ 150 as compared to ≈ 50 for $g_{MJ(r)}$ rdf. At $\beta = 6$ the contact value is ≈ 100 as compared to ≈ 10 for macroion-monovalent counterion rdf.



Figure(3.32) Macroions-Trivalent counterion radial distribution function for 60:2 (Z=2) system at β =0,0.2,1 and 6

The macroion-coion radial distribution function rdf is given in figure 3.33 at $\beta = 0.2$, 0.4, 0.8, 1, and 6. We note that at $\beta = 0.2$, 0.4 small β the coions are expelled from the macroions vicinity. This effect becomes less pronounced at $\beta = 0.8$,1, and 6. The location of the maximum corresponds to a separation from the macroion surface sufficient to accommodate a monolayer of counterions in between.

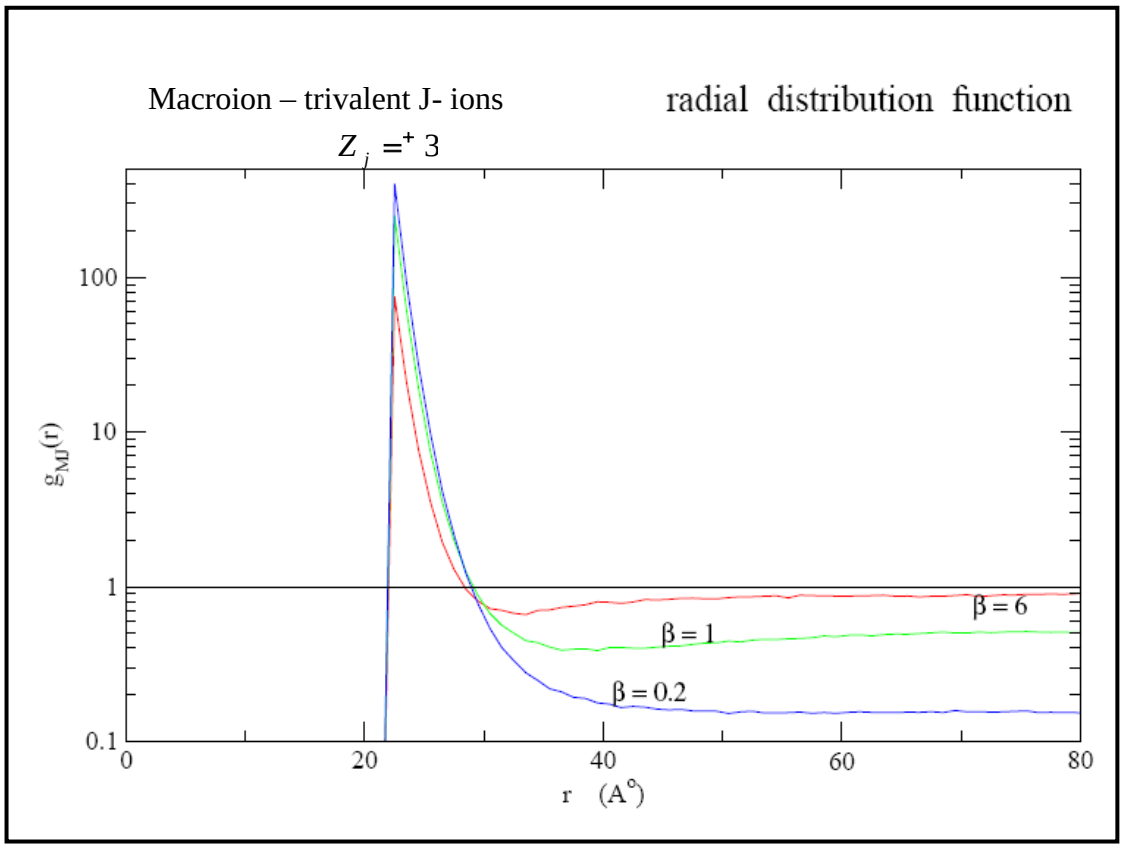


Figure(3.33) Macroion-Coion radial distribution function for 60:2(Z=2) system at β =0.2,0.4,0.8,1, and 6

At $\beta = 0.8$, the coions are more uniformly distributed than the rest of β's except for an enhanced local density about $r \approx 28A^{\circ}$.

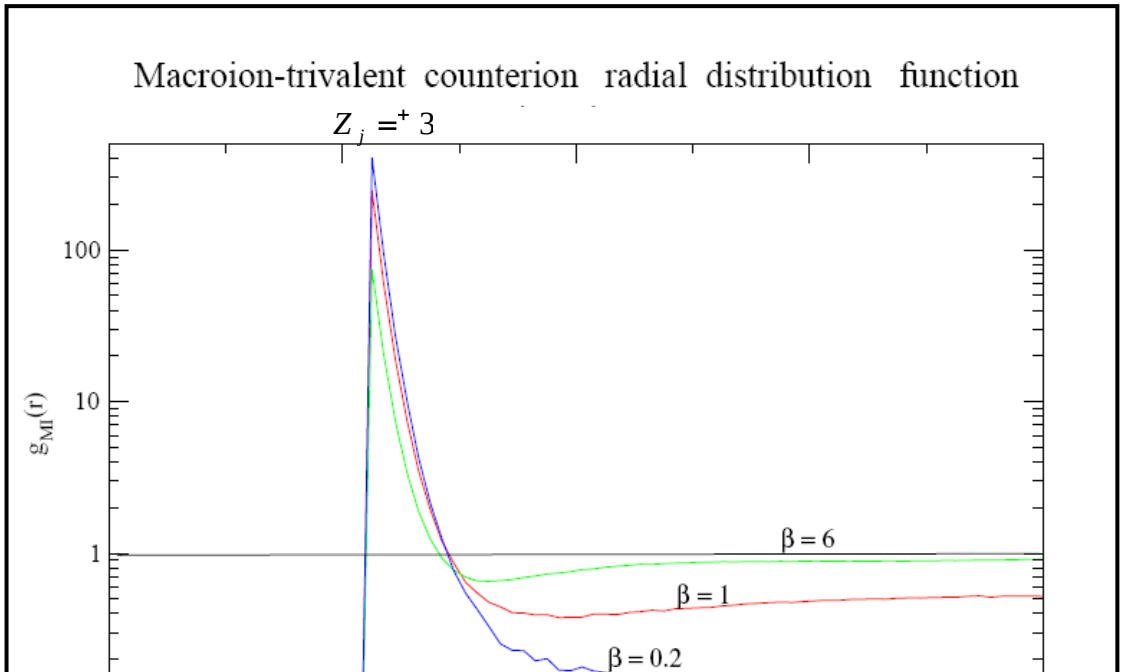
3.4.3 60:3 $(Z_j = +3)$ system

In the case of 60:3 system the radial distribution functions rdf's of small ions of a function of distance (r) from the macroion are discussed at different salt added concentration. The macroion-monovalent counterion (J-ions) radial distribution functions $g_{MI}(r)$ displayed in figure 3.34 at $\beta = 0.2$,1 and 6. They have as in 60:1 and 60:2 systems maxima at the hard-sphere contact separation $r = R_M + R_J = 22A^{\circ}$, clearly demonstrating the accumulation of the counterions near the macroions. At $\beta = 0.2$, 1, and 6 the contact value are ≈ 180, 150, and 100 respectively. The contact value decrease as β increased. The contact values of $\beta = 0.2$,1, and 6 have the most magnitudes in 60:3 system as compared to 60:1 $(Z_j = +1)$ and 60:2 $(Z_j = +2)$ systems.



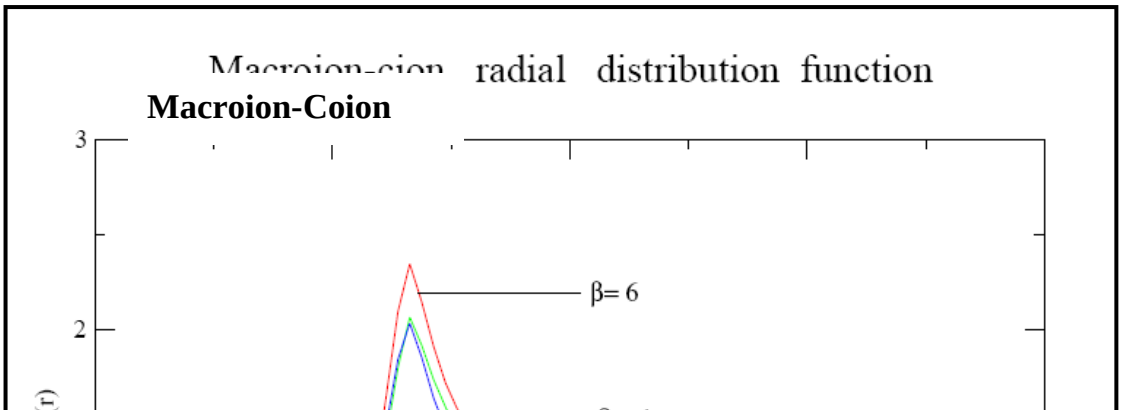
Figure(3.34) Macroions-monovalent counterion radial distribution function for 60:3 (Z=3) system at β =0,0.2,1 and 6

Figure 3.35 shows the strong accumulation of the trivalent counterions near the macroions. At $\beta = 0.2$, 1, and 6 the contact values is ≈ 800, 500, and 100 respectively. The contact values are similar to for the macroion-monovalent counterion radial distribution function.



Figure(3.35 Macroions-Trivalent counterion radial distribution function for 60:3 (Z=3) system at β =0,0.2,1 and 6

The macroion – coion radial distribution function at $\beta = 0.2$, 1, and 6 are given in figure 3.36. We note that at low salt concentration , $\beta = 0.2$ and 1, the coions don't expelled from the macroions vicinity as in 60:1 and 60:2 systems. The contact value of $\beta = 6$ is more than of 60:1 and 60:2 systems.



Figure(3.36) Macroion-Coion radial distribution function for 60:3(Z=3) system at β =0.2,0.4,0.8,1, and 6 .

Finally, we have noted that the monovalent counterions accumulated near the macroion are replaced by trivalent counterions when the latter are added. The appearance of remaining local density maximum of monovalent counterions at macroions contact and of local density maximum of coions are due to correlations effect.

All atomic and molecular details that may be important in real systems are suppressed. For example, the discrete nature of water molecules, being important for interaction at short separation is neglected. Second, the complexity of having regions with different dielectric permeability is also neglected. In micellar solution, the interior of the micelle has smaller dielectric permeability leading to additional repulsive force acting at short separation between charge and macroion.

Chapter Four

Conclusion and Summary

4.1 Conclusion

4.1.1 Salt-Free System

The Salt-Free 60:1, 60:2, and 60:3 model system used have thoroughly been characterized in terms of structural and thermodynamic properties. Briefly, simulations of these systems have shown that, firstly the 60:1 system is stable and possessing a long-range order with well separated macroions characteristic of strongly repelling objects. Secondly the 60:2 system displays no long-range ordering and a weak tendency for formation of macroion pairs. Thirdly the 60:3 system is unstable and separates in two phases, one dense and one dilute with respect to the electrolyte (4).

The properties of the 60:1 system is well described by the electrostatic part of the classical DLVO theory, provided that scaled macroion charges are employed. The repulsion can be viewed as arising from partly overlapping electrical double layers(4). Regarding the 60:2 and in particular the 60:3 systems, additional short-range attractions originating from spatial correlations of ions residing near different macroions come into play. This is an effect that is not captured by the DLVO theory.

4.1.2 Effect of Salt:

With monovalent counterions only, strong repulsion appeared between macroions, corresponding to a stable solution. As trivalent counterions are added, the mean force becomes less repulsive and eventually attractive with the maximal attraction appearing at stoichiometric amount of added trivalent counterions. As observed, the mean force of the 60:1 system at $\beta = 1$ is very similar to that of the 60:3 salt free system, which is unstable. Hence, the 60:1 at $\beta = 1$ is also unstable.

In large excess of salt, the mean force is still attractive, but considerably weakened. Thus, we infer that, as trivalent counterions are added, the model system passes through the following stages (i) stable solution (ii) a two-phase region, and (iii) a redissolution, which are in agreement with the experimental results found for the $\boldsymbol{SDS - Al\left(NO_3\right)_3 - H_2O}$ ternary system (4).

We notice that as trivalent counterions are added, the nature of the mean force changes continuously from being pure repulsive to being attractive at short separation and finally purely attractive. The mean force of 60:1 system at $\beta = 1$ is similar to that of the 60:3 system. This was understood from the fact that the 60:1 system with stoichiometric amount of 1:3 electrolyte could equally well be viewed as a 60:3 system with stoichiometric amount of 1:1 electrolyte. Moreover the simulations using the spherical cell showed a nearly uniform distribution, only a weak accumulation near the macroion was observed. Hence, the role of the monovalent counterion and coions is to provide only a weak interactions.

The structural changes upon addition of the simple 1:3 salt to the 60:1, 60:2, and 60:3 solutions in the range from $\beta = 0$ to 6 can also be interpreted as follows. With monovalent counterions only, a large fraction of them are accumulated near the macroions due to the attractive macroion- counterion interaction. The degree of accumulation is a balance of this attraction and mixing entropy, the latter favoring a uniform counterion distribution. Owing to the stronger electrostatic attraction to the macroion, the trivalent counterions replace the monovalent ones as the trivalent counterions are added. Simultaneously, the electrical double layer becomes thinner reducing the double-layer repulsion. In the force analysis presented, the appearance of the attraction is a combination of a strong reduction of the ideal repulsion, owing to the reduction of the number of small ions in the region between the macroions, and an electrostatic attraction across the mid-plane.

In the case of large concentrations of salt $\beta \geq 1$, a gradual reduction of the attractive mean force was observed. On a sample level of description one could argue that the attraction, which is of electrostatic origin, is reduced due to a screening by the increased electrolyte(4).

The three components of mean force in the range from $\beta = 0$ to 6 can also interpreted as follows.

At $\beta \geq 1$, $F_{ideal} + F_{hs}$ is repulsive and F_{elec} attractive with the net force being small as compared to the magnitude of these two terms at high salt concentration. The reduced

attraction as β is increased arises from the fact that the sum $F_{ideal} + F_{hs}$ grows faster than $\left|F_{elec}\right|$. The increase of $F_{ideal} + F_{hs}$ is due to an increased number of small ions in the region between the macroions which increases more rapidly than at the cylinder ends. The decrease of F_{elec} is owing to the cohesiveness of the Coulomb interaction.

As trivalent salt was added, it was found from analysis of the structure factor at small wave length that the stability of the solution was reduced. With an excess of the salt the stability was however regained.

We have noted the attractive force magnitude of like charged macroions is greater than of unlike charge macroions.

4.2 Summary

On the Monte Carlo simulations involving a cylindrical cell model containing two macroions representing DS-surfactant micelles, the mean force acting between them has been obtained at different conditions. In the absence of additional salt, the repulsive mean force appearing with monovalent counterions is reduced and becomes eventually purely attractive as the counterion are replaced with divalent and finally with trivalent ones.

As trivalent counterions are added in the 60:1, 60:2, and 60:3 systems. The magnitude of the attractive mean force starts to decrease. On the basis of previous connections established between the mean forces and the phase stability of identical model systems, we argue that the present model results give account for some salient features recently observed on SDS micelles as $Al\left(NO_3\right)_3$ is added. The three main points are the sequence of (i) stable solution, (ii) a two-phase region, and (iii) a redissolution as the amount of trivalent counterions is increased. The strongest attraction appeared near stoichiometric amount of trivalent counterions.

The present work provides additional evidences on the appearance of attractive forces between like-charged and unlike-chaged colloids induced by multivalent counterions in aqueous solutions (4).

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